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Kinetic Models in Heterogeneous Catalysis

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The role and importance of chemical kinetics in heterogeneous catalysis at the present stage of development are examined and the concept of kinetic models, in the exact, reliable, complete, and well-founded form, as well as the usefulness of combined kinetic investigations for the determination of these models are discussed. The effectiveness of combining different methods for devising informative models of this kind, examples of which are quoted, is demonstrated. The problems involved in setting up non-steady-state kinetic models, which are some of the most important in chemical kinetics, are briefly described. The optimum characteristics of kinetic models and the relation between the properties of the latter and the characteristics of reaction selectivities are analysed. The kinetic aspects of tests of the activities and selectivities of catalysts of complex reactions are mentioned in conclusion.

The bibliography includes 202 references.

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I. INTRODUCTION

The principal trend in theoretical research into heterogeneous catalysis is the determination of a relation between the properties of the surface layer of catalysts and the characteristics of the processes which they accelerate. Progress in this direction requires a profound understanding of the time course of catalytic processes, which determines the status of chemical kinetics in heterogeneous catalysis and gives rise to the idea of its "kinetic foundation".

Although the creation of such foundation was begun by the early investigations of Langmuir, Hinshelwood, and Schwab, the role and importance of the kinetics of heterogeneous catalytic reactions became evident only comparatively recently, this being promoted by the factors listed below:

(1) The spread of accurate kinetic experimental techniques[1-3], which make it possible to obtain reliable data without the distorting influence of factors which were previously not taken into account.

(2) The development of a theory of complex reactions[4-6] whereby one can approach an understanding of the kinetics without undue simplifications.

(3) The extension of the theory of macrokinetics to permit the estimation of transport parameters in the course of reactions and the inclusion of real process conditions[7,8].

(4) The employment of computer techniques and the increase in the scope of the mathematical analysis of kinetics and kinetic problems[9-11]. The operation of these factors clearly established the role of chemical kinetics as a science and the possibility of its theoretical employment to establish one of the necessary procedures for the elucidation of the mechanisms of catalytic reactions as well as its practical employment in one of the stages of the incorporation of the technology of catalytic processes in industry and its improvement. Table 1 gives a brief compilation of processes for which reactors have been simulated in recent years and the optimum conditions analysed on the basis of kinetic data[12-40]. In Boudart's review[41], a greater importance is already attributed to the practical aspects of the employment of kinetics than to its theoretical aspects. However, both aspects of the problem are so closely interrelated and inseparable that preference should not be given to either.

Table 1. Examples of processes for which modelling and optimisation have been carried out using kinetic data.

Process and catalyst	Result	Refs.
Selective hydrogenation of phenol; Pd	Calculation of optimum conditions for the operation of reactor	12
Selective hydrogenation of ethynyldimethylmethanol; Pd	Reactor model	13
Liquid-phase hydrogenation of heptene; Ni	Analysis of reactor model	14
Conversion of glucose into glycerol; Ni	Optimum reactor design	15
Reduction of nitrobenzene; Cu	Calculation and selection of reactor dimensions	16
Hydrogenation of dichloronitrobenzene to dichloroaniline; Pt	Reactor design	17
Hydrogenation of fats on different catalysts	Design of large-scale apparatus	18
Dehydrogenation of butane and butene; Al–Cr	Optimum conditions	19
Dehydrogenation of isopentenes to isoprene; Ca–Ni–P	Optimum conditions	20
Dehydrogenation of ethanol; Cu	Optimum conditions	21
Oxidative dehydrogenation of butenes; Zn–Cr–Fe	Modelling of an adiabatic reactor	22
Oxidation of propene; Co–Mo	Optimum diameter of a tubular reactor and process parameters	23
Oxidation of benzene to maleic anhydride; V_2O_5	Calculation of reactor model parameters	24
Oxidation of *o*-xylene; V_2O_5	Reactor model and optimum conditions	25,26
Oxidation of naphthalene in a fluidised bed; V_2O_5	Reactor model	27
Oxidation of methanol; Ag	Reactor model and optimum conditions	28
Oxidation of anthracene; V_2O_5	Calculations on reactor operation	29
Oxidative chlorination of ethylene in a fluidised bed; $CuCl_2$	Calculations of the parameters and optimum conditions	30
Extensive oxidation of pentane; Al–Pt	Reactor model and optimum conditions	31
Extensive oxidation of phenol; Al–Pt	Optimum reactor design, analysis of stability	32
Extensive oxidation of methyl methacrylate; Al–Pt	Reactor conditions, analysis of stability	33
Oxidation of HCl in a fluidised bed of chlorides, Cu, Sn, and K	Analysis of reactor operation	34
Oxidation of sulphur dioxide; V_2O_5	Optimum reactor model	35
Conversion of CO by water vapour, Fe–Cr and Cr–Sn	Optimum parameters of the reactor for a two-stage process	36
Conversion of methane by water vapour; Ni	Optimum parameters of a tubular reactor	37
Hydrochlorination of acetylene on Hg_2Cl_2	Process optimisation and calculation of reactor parameters	38
Dehydration of α-hydroxyisobutyric acid on calcium phosphate	Calculation of reactor parameters	39
Demethylation of toluene by water vapour; Rh–Al	Calculation of the parameters of a cascade of reactors	40

The central task of kinetics in heterogeneous catalysis at the present stage is the creation of kinetic models of various catalytic processes and a comparison and generalisation of these models. This task is particularly urgent in the light of the fact that further development of catalysis at the present time can apparently involve primarily the elucidation and accumulation of special and general relations rather than the creation of new universal theories.

On the basis of the foregoing, we shall consider the problem of kinetic models in heterogeneous catalysis and the extent to which it can be described by these models. Ways for the effective creation of kinetic models and certain problems associated with the properties of the models and the characteristics of catalytic processes will be discussed.

II. CHARACTERISTICS OF KINETIC MODELS

A quantitative characteristic of a process in the form of a mathematical description of its velocities (in the presence of a given catalyst) in the different directions realised under specified conditions, based on multistage mechanisms reflecting the general characteristics of the reaction, and carrying the necessary information about the catalyst and about significant non-steady-state changes as a function of different factors, will be regarded as a kinetic model. Multistage mechanisms (proved or hypothetical) indicate the sequence and stoichiometry of the transformations of the intermediate compounds. The availability of data for the ratios of the rates of the stages under the conditions investigated permit simplifications in the complete mathematical description of the rate of the process. In considering a kinetic model, we can speak of its form, implying by this a mathematical description of the rate of the process and the factors influencing it (including factors causing a change in the activity of the catalyst) and of the content of the model, i.e. the characteristic features which give rise to the given form.

Such traetment of the concept of the kinetic model differs significantly from the concept of reaction mechanism—the comprehensive qualitative characteristic of its internal features in the presence of the given catalyst under the specified conditions, reflecting the nature of the intermediate species produced at the elementary stages as well as their coupling. In the kinetic model, the principal factor is tested and detailed information about the changes in the rate of the process, while in the concept of reaction mechanism the main factor is detailed information about the nature, properties, and interconversions of the intermediates. The simplest step in the change of the chemical state of the system, involving the overcoming of not more than one energy barrier corresponding to the formation and decomposition of a single activated complex, must be regarded as an elementary stage.

In its broad sense, the kinetic model serves as a most important process characteristic, which may be tabulated for a given catalyst under specified conditions. The model must therefore be exact, reliable, complete, and well-founded. The accuracy of the kinetic model is determined primarily by the accuracy of the experimental methods used to establish it. Gradient-free methods[1-3], which make it possible to obtain accurate kinetic data under steady-state conditions, are nowadays generally accepted for this purpose. They can be supplemented by non-steady-state methods for the elucidation of the influence of the reaction system on the catalyst, the characteristics of its activation, and the changes in the activity and behaviour of the catalyst under non-steady-state conditions[42,43]. The reliability of the model depends not only on the experiment but also on its treatment and interpretation, taking into account all the factors influencing the kinetics, and

Table 2. The ambiguity of certain kinetic equations and process mechanisms.

Reaction	Kinetic equation	Multistage mechanism	Remarks
Hydrochlorination of acetylene on $HgCl_2$ (Ref.53)	$r = k \frac{P_{C_2H_2} P_{HCl}}{1 + k'P_{C_2H_2} + k''P_{HCl}}$ $r = k \frac{1 + k' (1 + k'' P_{HCl}) P_{C_2H_2} P_{HCl}}{(1 + k_1 P_{HCl}) (1 + \frac{k_2 P_{C_2H_2}}{1 + k_3 P_{HCl}} + k_4 P_{HCl})}$	—	Both equations describe kinetic data equally well
Hydrogenation reaction $A + H_2 = AH_2$ (Ref.54)	$r = k P_A^{1-m} P_{H_2}$	I. 1) $A = A_{ads}$; 2) $A_{ads} + H_2 = AH_2$(slow) II. 1) $H_2 = 2H_{ads}$; 2) $2H_{ads} + A = AH_2$(slow) III. 1) $A + H_2 + [K] = A[K] \cdot H_2$ (slow) 2) $A[K] \cdot H_2 = AH_2 + [K]$	All three mechanisms lead to the same kinetic equation
Conversion of methane by water vapour (Ref.55)	$r = k \frac{P_{CH_4} P_{H_2O} \gamma}{P_{H_2O} + k_1 P_{H_2} + k_2 P_{H_2}^2 + k_3 P_{H_2}^3}$ (γ = correction for effect of reverse reaction)	"Oxidative mechanism" 1) $CH_4 = CH_{2ads} + H_2$ 2) $CH_{22ads} + H_2O = CHOH_{ads} + H_2$ 3) $CHOH_{ads} = CO_{ads} + H_2$ 4) $CO_{ads} = CO$ "Dehydrogenation mechanism" 1) $CH_4 = CH_{2ads} + H_2$ 2) $CH_{2ads} = C_{ads} + H_2$ 3) $C_{ads} + H_2O = CO_{ads} + H_2$ 4) $CO_{ads} = CO$	The same kinetic equation corresponds to both mechanisms

on the choice of the most adequate and unambiguous mathematical description of the process. Numerous methods involving the use of computers and experimental design have been developed for this purpose[10,11,44-51]. The completeness of the model depends on the width of the range of variation of the process conditions under which it is investigated and on the allowance for all possible pathways contributing to the observed features. Secondary pathways are frequently significant under these conditions (even when their contribution to the overall rate of the process is slight; see, for example, Spivak et al.[52]); also important is allowance for non-steady-state transitions (including those due to changes in the catalyst activity), the influence of the reaction mixture on the composition of the surface layer, the blocking of the surface by coke or other substances, etc. Depending on the purpose of the models, their completeness may be various. Finally, in order to prove the validity of kinetic models it is desirable that other physicochemical methods as well as kinetic methods should be used in devising them. This is because the application of kinetic experimental techniques and kinetic computational procedures alone can frequently lead to ambiguous models, examples of which are illustrated in Table 2. The examples[53-55] show that kinetic data, even those obtained by exact methods over a wide range of variation of conditions, can be described equally well by different fairly complex equations. On the other hand, various mechanisms and hence various multistage schemes can correspond to the same simple or complex kinetic equation.

Although numerous new physical methods, which can be used successfully (although still insufficiently) in catalysis for the elucidation of the nature of the intermediate species (see, for example, McCarroll[56]) have become available in recent years, the results obtained with their aid but without kinetic justification can also prove to be ambiguous. An example is provided by the decomposition of formic acid. The conclusion had been reached previously on the basis of infrared spectroscopic and adsorption studies[57,58] that the dehydrogenation of formic acid in the presence of nickel proceeds via the formation and slow decomposition of a surface formate. In a later study[59] it was shown (by combining the same measurements with kinetic data) that the rate of reaction decreases with increasing concentration of the surface formate. This introduces significant corrections to the earlier mechanism (the reaction proceeds on the part of the surface which is not blocked by the formate, apparently via the formation and decomposition of carboxylate complexes).

Conclusions reached solely on the basis of kinetic studies, even as regards the slow stage of the process, can be equally unreliable. Thus a study of the kinetics of the hydrogenation of cyclohexene in the presence of nickel and calculations of the absolute reaction rate led to the conclusion[60] that the process proceeds via a slow surface interaction of the two components. However, the present author's investigations[61,62] (where isotope exchange in cyclohexene and cyclohexane was studied in addition to reaction kinetics, measurements were made of the kinetic isotope effects, and the rates of the individual stages were compared using the ^{14}C label) showed that the process proceeds via the slow formation of a surface compound of cyclohexene followed by its rapid interaction with hydrogen†.

Thus in the general case, the kinetic model must not be justified by kinetic data alone, while, on the other hand, the corresponding reaction mechanism and the corresponding multistage schemes cannot be reliably established solely by means of the pyhsicochemical methods designed for this purpose without combining them with kinetic measurements. Hence the kinetic foundation

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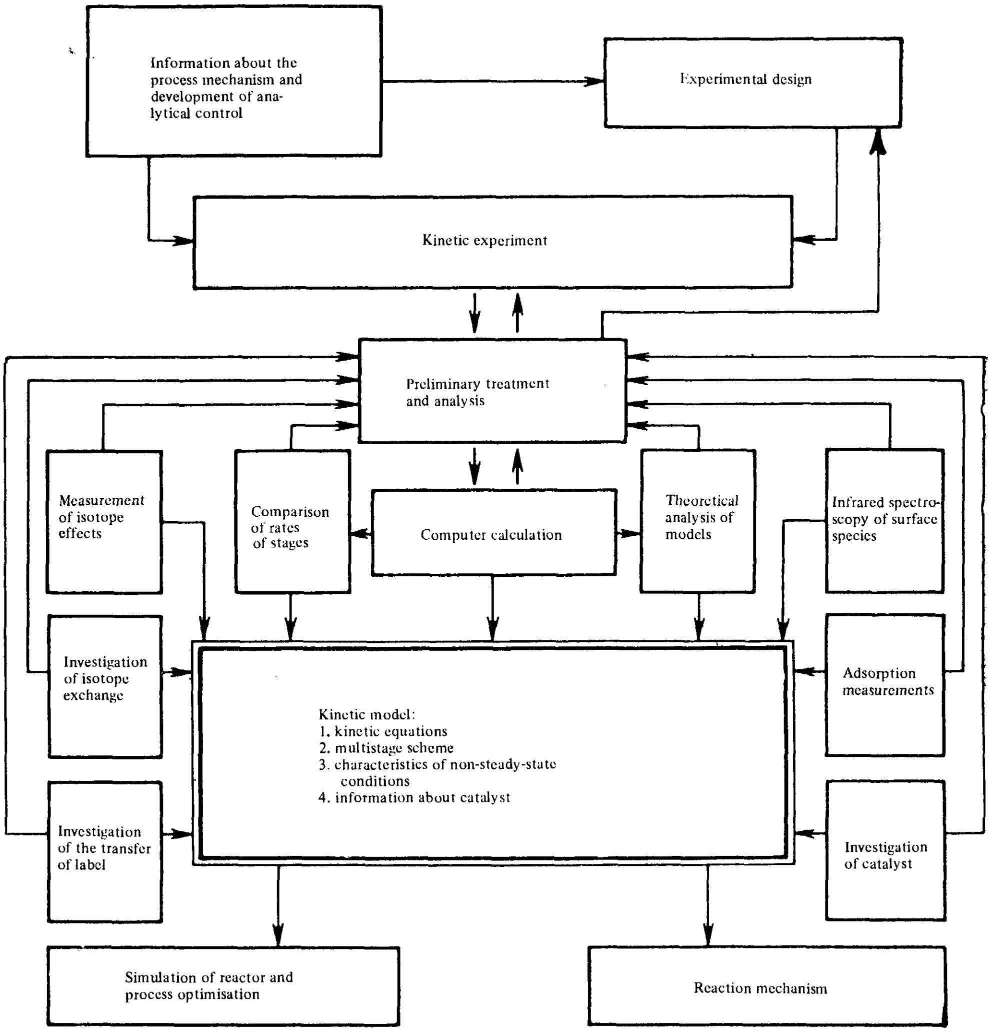
†The present authors data were obtained at higher temperatures than those of Erkelens and Ejkema[60], but, since the slow chemical adsorption stage cannot become rapid on decreasing the temperature, it is hardly likely that another stage becomes rate-limiting.

requires a physicochemical support and for this reason it is desirable to carry out complex kinetic studies in which accurate kinetic and other physicochemical measurements are combined‡.

Scheme 1

Formulation of complex kinetic studies



Such combination of procedures (particularly when kinetic, isotope, adsorption, and spectroscopic methods are used, especially under the conditions of the reaction investigated) may be effective in obtaining information about kinetic models. Measurements of kinetic isotope effects and the study of isotope exchange in the reaction components yield particularly valuable information about the role of the possible stages and intermediate species. On the other hand, spectroscopic studies yield more information when they are combined with kinetic measurements, which also reduces the risk of adopting as the main ones the intermediate forms of the "blind end" compounds responsible for secondary reaction pathways (see above). Scheme 1 illustrates the formulation of complex kinetic studies. Kinetic models devised in this way can be justified and can be made to yield much information by making sure that the model corresponds to the specified set of results. Evidently, such models are preferable to those obtained on the basis of kinetic measurements alone.

Only a few kinetic models obtained on the basis of complex investigations are described in the literature. Some of them, described in recent publications, may be mentioned. The kinetics of the isomerisation of but-1-ene and but-2-ene in the presence of a magnesium oxide catalyst have been investigated[63] at 26°C. At the same time, a study was made of the adsorption of the reaction components and the infrared spectra of the surface species and the ESR spectra of the catalyst were obtained. The results were described by a first-order kinetic equation which was derived on the basis of a multistage mechanism

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‡Here and henceforth we shall use the term "complex kinetic studies" emphasising thereby that kinetic measurements are the fundamental feature.

presupposing the physical adsorption of the initial substance with its slow conversion into the *cis*- and *trans*-isomers of but-2-ene simultaneously and their desorption.

A kinetic model for the dehydrogenation of isobutane to isobutene in the presence of an alumina–chromium oxide catalyst was obtained[64,65] in the temperature range 380 to 575°C. Apart from kinetic measurements, a study was made of the transfer of the radioactive carbon and deuterium labels[64] and a comparison was made of the rate of the process with the rate of the para-ortho conversion of hydrogen in order to determine the ratio of the rates of the stages[65]. A first-order kinetic equation satisfying the mechanism in which the slow stage is the formation of the surface compound C_4H_{10ads} was obtained in both investigations.

The kinetics of the hydrogenolysis of cyclopropane in the presence of a nickel catalyst at 60°C have been investigated[66] and at the same time a study was made of the adsorption of the components and of their isotope exchange with deuterium. The rate of reaction r with formation of propane as well as ethane and methane was described by the kinetic equation

$$r = k\frac{P_1}{1 + k'P_1}, \tag{1}$$

where P_1 is the partial pressure of the initial substance and k and k' are constants. The author justifies it by a scheme according to which a C–C bond in the adsorbed cyclopropane is dissociated on the surface with formation of adsorbed propene. The latter either combines with hydrogen (to form a surface propyl and then propane) or undergoes further hydrogenolysis to ethyl and methyl fragments.

In a study of the kinetics of the reaction of carbon monoxide and nitric oxide in the presence of copper(II) oxide at 135–200°C, i.e.

$$2CO + 2NO = 2CO_2 + N_2 \quad , \tag{2}$$

London and Bell[67] also obtained the infrared spectra of the surface species and studied the catalyst. They derived the kinetic equation

$$r = k\frac{P_{NO}}{(1 + k_1P_{NO} + k_2P_{N_2O})(1 + k_3P_{CO})}, \tag{3}$$

which corresponds to a scheme presupposing the following transformations:

$$NO_{gas} \rightarrow NO_{ads} \rightarrow (N_{ads} + O_{ads}) \xrightarrow{+NO} \rightarrow N_2O_{gas} \rightarrow NNO_{ads} \rightarrow O_{ads} + N_2 \xrightarrow{CO} CO_2.$$

Earlier, Apel'baum and Temkin[68] combined a careful kinetic study of the hydrogenation of ethylene on palladium with the use of the catalyst in the form of a membrane permeable to hydrogen. This enabled them to describe the kinetic data in terms of a scheme involving the interaction of the adsorbed ethylene with gaseous hydrogen followed by the slow interaction of the surface ethyl radical with adsorbed atomic hydrogen (Twigg's mechanism).

Many models devised by the present author and his coworkers for different classes of gas-reactions will be briefly considered below mainly from the standpoint of the information obtained for the construction of models from a combination of exact kinetic studies in gradient-free systems with other physicochemical methods. Kinetic equations were derived for the resulting multistage mechanisms using hypotheses concerning processes on inhomogeneous catalytic surfaces[1].

III. KINETIC MODELS OF CERTAIN REACTIONS OBTAINED BY COMPLEX INVESTIGATIONS

1. Hydrogenation Reactions

(a) Selective Hydrogenation of Diolefins. The investigations were based on the hydrogenation of isoprene to isopentenes in the presence of a palladium–lead catalyst at 58–118°C.[69-71]. The rate of reaction r is described by the equation

$$r = kP_1^{0{,}5}P_{H_2}, \tag{4}$$

where P_1 and P_{H_2} are the partial pressure of the substance hydrogenated and hydrogen respectively. This equation is valid for the formation of each isopentene isomer separately, so that products with different structures arise from intermediate species without a subsequent bond redistribution. This is confirmed by the finding that, when isoprene reacts with deuterium, the degree of isotope exchange in the resulting isopentenes is slight {there is only a small amount of substituted $[D_1]$ and $[D_3]$ derivatives apart from the main addition $[D_2]$ product}. In this case kinetic isotope effects amount to 1.5–1.6, which indicates the involvement of hydrogen in the slow stages. The degree of isotope exchange in the initial isoprene is also low: hence it follows that the formation of the semi-hydrogenated form cannot be rapid.

Infrared spectroscopic study of the surface compounds produced in the reaction showed that the semihydrogenated form generated is strongly retained by the main part of the surface and only a small proportion (20–30%) is converted into the hydrogenation product under the reaction conditions. Experiments on the thermal desorption of hydrogen showed that it is strongly retained by the catalyst, passing into the gas phase only at high temperatures than those used in the reaction. However, this did not permit the conclusion that only the gas-phase hydrogen reacts, but it did indicate the probable nature of the relevant pathway. The combination of results led to scheme 2.

Scheme 2

Stage	Stoichiometric numbers of stages via different pathways		
	I	II	III
1. $C_5H_{8gas} = C_5H_{8ads}$	1	1	1
2. $C_5H_{8ads} = C_5H_{7ads} + H_{ads}$(slow)	0	0	1
3. $C_5H_{8ads} + H_{2gas} = C_5H_{9ads} + H_{ads}$(slow)	1	1	0
4. $C_5H_{9ads} + H_{2gas} = C_5H_{10gas} + H_{ads}$(slow)	0	1	0
5. $C_5H_{7ads} + H_{2gas} = C_5H_{9ads}$	0	0	1
6. $C_5H_{9ads} + H_{ads} = C_5H_{10gas}$(slow)	1	0	1
7. $2H_{ads} = H_{2gas}$	0	1	0

The reaction proceeds mainly via pathways I and II, with rapid formation of a surface isoprene compound and its slow interaction with gaseous or surface hydrogen. Pathway III takes into account isotope exchange.

A kinetic equation agreeing with experimental Eqn. (4) follows from Scheme 2. The combination of Eqn. (4) and scheme 2 constitutes the kinetic model of the process.

(b) Selective hydrogenation of acetylenic compounds. Reactions of this class were studied in relation to the hydrogenation of ethynyldimethylmethanol to dimethylvinylmethanol in the presence of a palladium–lead catalyst at 143–258°C [13,72,73]:

$$(CH_3)_2C(OH)C{\equiv}CH + H_2 = (CH_3)_2C(OH)CH{=}CH_2 \ . \tag{5}$$

The hydroxy-group is unaffected during the reaction, so that the starting compound is henceforth designated by RC≡CH, where R = $(CH_3)_2C(OH)$. The rate of the process is described by the kinetic equation

$$r = k\frac{P_1 P_{H_2}}{(P_1 + k'P_{H_2}^{0,5})^{-2,1}}\quad . \tag{6}$$

The specific features of this equation are reflected by the maximum in the "conversion curves"[48] relating r to the degree of conversion x. The kinetic isotope effect in the replacement of H_2 by D_2 amounts to 1.8–1.9, which indicates the involvement of hydrogen in the slow stages.

The study of the interaction of the initial alcohol with deuterium by mass-spectrometric, infrared spectroscopic, and NMR methods yielded interesting information. It was found that substitution in the hydroxyl and in the methyl group does not take place at all and the degree of exchange of α-hydrogen in the initial alcohol does not exceed 14%, being more pronounced in the resulting dimethylvinylmethanol but occurring without the involvement of the gas phase, i.e. solely as a result of the redistribution of H and D among the reaction components. Thus it follows from the isotope exchange data that the hydroxy-group in the alcohol is not subject to the influence of the surface, apparently because it is remote from the latter owing to the rigidity of the molecule. The absence of isotope exchange between the gas phase and dimethylvinylmethanol, whose molecules should no longer be rigid, shows that the latter is not retained by the surface in the presence of the initial alcohol, passing immediately to the gas phase. The small contribution of the isotope exchange involving the acetylenic alcohol shows that its interaction with hydrogen is not the rapid reaction stage.

Combination of the results leads to Scheme 3 in which the first pathway predominates:

Scheme 3

Stage	Stoichiometric numbers of stages via different pathways		
	I	II	III
1. $HC = CR_{gas} = HC = CR_{ads}$	1	1	1
2. $H_{2gas} = 2H_{ads}$	1	0	0
3. $HC = CR_{ads} + 2H_{ads} = H_2C = CHR_{gas}$(slow)	1	0	0
4. $HC = CR_{ads} + H_{2gas} = H_2C = CHR_{gas}$(slow)	0	1	0
5. $HC = CR_{ads} + H_{2gas} = HC = CHR_{ads} + H_{ads}$(slow)	0	0	1
6. $HC = CHR_{ads} + H_{ads} = H_2C = CHR_{gas}$(slow)	0	0	1

This scheme leads to a kinetic equation agreeing with experimental Eqn. (6). Evidently the kinetic models of the two reactions considered above differ significantly in the presence of the same catalyst.

(c) Hydrogenation of Aromatic Hydrocarbons. Kinetic models have been obtained[74-80] for the hydrogenation of benzene and toluene in the presence of a nickel oxide–zinc oxide catalyst at temperatures up to 270°C, mainly in the region where the processes are reversible. The rates of both reactions pass through a maximum at 180–190°C and the region where the reactions are reversible corresponds to the descending sections of the r–T curves, the decrease of the reaction rate with increasing temperatures being unrelated to the approach to equilibrium and being caused by the process mechanism. The kinetics of the two reactions in the region of reversibility are described by the equation

$$r = kP_1^{0,5}P_{H_2}^{3}\gamma, \tag{7}$$

where γ is the multiplier taking into account the influence of the reverse reaction[81]. Kinetic equations for the forward[82] and reverse[83-85] processes have been obtained separately for the hydrogenation of benzene, the equation for the reverse reactions being

$$r = kP_{C_6H_{12}}P_{C_6H_6}^{-0,5}. \tag{8}$$

In the region of low conversions at low pressures $P_{C_6H_{12}}$ (up to 0.1 atm) another equation is valid for the rate of dehydrogenation of cyclohexane:

$$r = kP_{C_6H_{12}}^{0,5}, \tag{9}$$

with increase of the partial pressure of C_6H_{12}, it is converted into a zero-order equation.

Comparison of the rates of hydrogenation of [^{14}C] benzene, cyclohexene, and cyclohexadiene (separately or jointly)[61] showed that, over the entire range of conversions, benzene reacts much more slowly, so that the transformations of C_6H_8 and C_6H_{10} in the hydrogenation of benzene cannot constitute the slow stage. Under these conditions, the rate of hydrogenation of cyclohexene in the presence of an excess of hydrogen is expressed by the equation

$$r = kP_{C_6H_{10}}P_{C_6H_{12}}^{-0,5}. \tag{10}$$

Comparison with the rate of the para-ortho conversion of hydrogen

$$para\text{-}H_2 = ortho\text{-}H_2 \tag{11}$$

under analogous conditions yields information about the contribution of the rates of adsorption and desorption of hydrogen to the overall rate of the process. It was found that the rates of hydrogenation of benzene and dehydrogenation of cyclohexane are much lower than the rate of reaction (11); consequently the adsorption and desorption of hydrogen cannot be the slow stages in the given process.

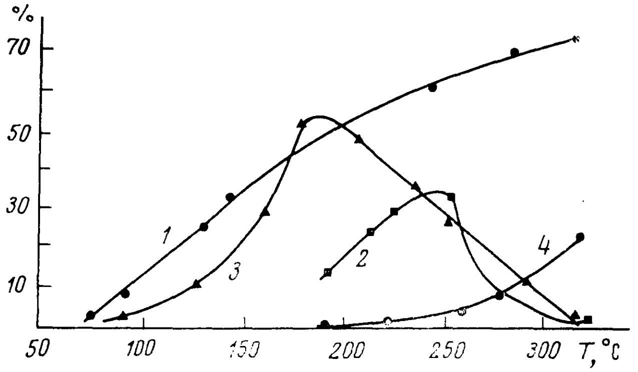

Figure 1. Temperature dependence of the degree of conversion in hydrogen–deuterium isotope exchange processes in benzene (curve *1*) and cyclohexane (curve *2*), the hydrogenation of benzene (curve *3*), and the dehydrogenation of cyclohexane (curve *4*) in the presence of a nickel oxide–zinc oxide catalyst.

Figs. 1–3 present the temperature variation of the rate of isotope exchange (proportional to the degree of conversion) between hydrogen and deuterium in the initial substances and in the products of the given reactions. Evidently, the rate of isotope exchange in benzene and toluene increases monotonically with temperature and greatly exceeds the rate of hydrogenation. On the other hand, the rate of dehydrogenation increases with temperature, while that of isotope exchange passes through a maximum, although in the region of the reversibility of the reaction it exceeds the rate of dehydrogenation. The rates of hydrogenation and dehydrogenation of cyclohexane are much higher than the rate of isotope exchange, which is extremely low.

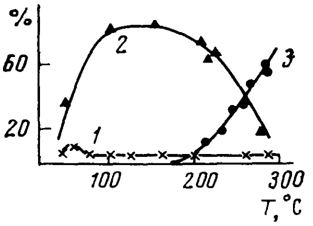

Figure 2. Temperature dependence of the degree of conversion in hydrogen–deuterium isotope exchange processes in cyclohexene (curve *1*), the hydrogenation of cyclohexene (curve *2*), and its dehydrogenation (curve *3*) in the presence of a nickel oxide–zinc oxide catalyst.

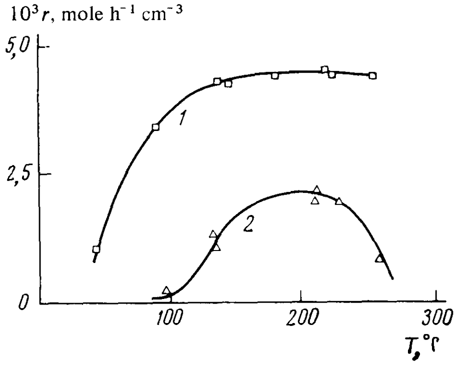

Figure 3. Temperature dependence of the rate of the hydrogen–deuterium isotope exchange in toluene (curve *1*) and the hydrogenation of toluene (curve *2*) in the presence of a nickel oxide–zinc oxide catalyst.

The exchange in toluene proceeds most readily when the methyl group is involved; the nature of the isotope distribution in the methylcyclohexane shows that the latter is not retained by the catalyst surface. Comparison of the rates of the ortho-para conversion of hydrogen on the clean catalyst surface and on the surface with adsorbed cyclohexane or cyclohexene[86] confirms the dissociative mechanism of the adsorption of cyclohexane. The study of the adsorption of benzene[87], the infrared spectra of the surface compounds, and ferromagnetic resonance[88,89] as well as quantum-chemical calculations[90] led to the conclusion that the benzene molecules assume a planar orientation with the probable formation of π-complexes. These results made it possible to rule out the possibility of slow adsorption and desorption stages in the hydrogenation of benzene and cyclohexane.

Measurements of the kinetic isotope effects β confirmed these conclusions. Table 3 lists the values of β obtained, expressed as the ratios k_H/k_D of the rate constants for the reactions before and after the substitution of protium by deuterium (the values of β may be distorted slightly owing to isotope exchange during the reaction).

Table 3. Kinetic isotope effects β in the substitution of H by D in the hydrogenation of benzene, cyclohexene, and toluene and in the dehydrogenation of cyclohexene.

T, °C	Reaction	β	*T*, °C	Reaction	β
240	$C_6H_6+3H_2=C_6H_{12}$ $C_6D_6+3H_2=C_6D_6H_6$	0.53	110	$C_6H_{10}+H_2=C_6H_{12}$ $C_6H_{10}+D_2=C_6H_{10}D_2$	0.99
240	$C_6H_6+3H_2=C_6H_{12}$ $C_6H_6+3D_2=C_6H_6D_6$	0.60	220	$C_6H_{10}+H_2=C_6H_{12}$ $C_6H_{10}+D_2=C_6H_{10}D_2$	1.02
240	$C_6D_6+3H_2=C_6H_6D_6$ $C_6D_6+3D_2=C_6D_{12}$	0.55	217	$C_6H_5CH_3+3H_2=C_7H_{14}$ $C_6H_5CH_3+3D_2=C_7H_8D_6$	0.39
240	$C_6H_6+3H_2=C_6H_{12}$ $C_6D_6+3D_2=C_6D_{12}$	0.28	217	$C_6H_5CH_3+3H_2=C_7H_{14}$ $C_6D_5CH_3+3H_2=C_7D_5H_9$	0.92
270	$C_6H_6+3H_2=C_6H_{12}$ $C_6H_6+3D_2=C_6H_6D_6$	0.51	217	$C_6H_5CH_3+3H_2=C_7H_{14}$ $C_6H_5CD_3+3H_2=C_6H_{11}CD_3$	1.10
293	$C_6H_{12}=C_6H_6+3H_2$ $C_6D_{12}=C_6D_6+3D_2$	2.3	217	$C_6H_5CH_3+3H_2=C_7H_{14}$ $C_6D_5CD_3+3H_2=C_7D_8H_6$	0.77
265	$C_6H_{12}=C_6H_6+3H_2$ $C_6D_{12}{}^*=C_6D_6+3D_2$	1.8	217	$C_6H_5CH_3+3H_2=C_7H_{14}$ $C_6D_5CD_3+3D_2=C_7D_{14}$	0.89
			250	$C_6H_6CH_3+3H_2=C_7H_{14}$ $C_6D_5CD_3+3H_2=C_7D_8H_6$	0.59

*A mixture of different deuterocyclohexanes.

Appreciable effects in the hydrogenation of benzene and toluene involving the replacement of protium by deuterium in the hydrocarbon and in the hydrogen molecule indicate the involvement of the two components in the slow stages. It is remarkable that the effects observed here are the opposite of those usually found (the rate of the process increases following substitution by the heavy isotope instead of decreasing in accordance with the postulate of the elementary theory of isotope effects[91–93]; on the other hand, the effects in the reverse reaction are normal). The present author explained this finding on the basis of the multistage nature of the process and the relative bond strengths in the initial substances and in the activated complexes[94].

The stoichiometric number ν of the rate-limiting stage[1,4,5] was calculated from the values of β for the forward and reverse reactions by Boreskov's method[95]. It proved to be unity, which rules out the possibility that the reaction proceeds via slow stages characterised by other stoichiometric numbers (for example, the absorption of hydrogen or a process proceeding via the disproportionation of intermediates[1,96]). Table 3 shows that there is no isotope effect in the hydrogenation of cyclohexene; consequently, hydrogen is not involved in the slow stage. The slow stage can only be the formation of a surface cyclohexene compound, which is also confirmed by isotope exchange data (see above).

Comparison of the rates of hydrogenation and isotope exchange for benzene and its alkyl derivatives showed that the rate of hydrogenation decreases steadily, while that of isotope exchange remains at approximately the same level. On the other hand, in cycloalkanes it depends significantly on the nature of the substitution[79,97].

A scheme for the hydrogenation of benzene and toluene, providing for the rapid formation of a surface π-complex of the hydrocarbon on the part of the surface weakly retaining molecularly adsorbed hydrogen, which does not hinder the adsorption of the hydrocarbon, was put forward on the basis of the complete set of results. Subsequently, there is slow interaction between the hydrocarbon and the surrounding molecules of the weakly bound hydrogen, which leads to the formation of a coordination complex retaining the features of a surface π-complex. This reaction stage virtually constitutes a rearrangement of the surface bonds. The complex formed undergoes rapid isomerisation as far as the cycloalkane (possibly also via other intermediate stages), as shown in Scheme 4.

Scheme 4

1. $H_2 = (H_2)_{ads}$
2. $C_nH_{2n-6} + (Ni) = C_nH_{2n-6}(Ni)$
3. $C_nH_{2n-6}(Ni) + 3(H_2)_{ads} = [C_nH_{2n-6}(Ni)] \cdot 3H_3$ (slow)
4. $[C_nH_{2n-6}(Ni)] \cdot 3H_2 = [C_nH_{2n-4}(Ni)] \cdot 2H_2$ (rapid isomerisation)
5. $[C_nH_{2n-4}(Ni)] \cdot 2H_2 = [C_nH_{2n-2}(Ni)] \cdot H_2$ (rapid isomerisation)
6. $[C_nH_{2n-2}(Ni)] \cdot H_2 = C_nH_{2n\,gas} + (Ni)$.

The isotope exchange in benzene and toluene under the conditions of their hydrogenation also proceeds via the formation of a π-complex, which is converted, in conformity with the dissociative π-complex substitution mechanism[98], into a σ-bonded intermediate compound with elimination of a hydrogen atom (H_{ads}).

Scheme 4 leads to kinetic equations agreeing with the experimental Eqns. (7)–(9). Analysis shows that the decrease of the reaction rate after the temperature maximum and the formally negative apparent activation energies obtained are due to the high heats of formation of the surface compounds (their estimate[99] for benzene gave values in the range 25–35 kcal mole^{-1}).

In the region of irreversibility, the rate of hydrogenation of benzene is described by other relations: the equation

$$r = kP_{H_2}^{0.5} \tag{12}$$

holds at 90–135°C, while the equation

$$r = kP_1P_{H_2} \tag{12a}$$

is valid in the range 150–180°C. Here the process mechanism changes significantly and the rate of reaction is apparently determined by the rate of formation of the intermediate compounds $C_6H_7(Ni)$ and $C_6H_8(Ni)$ respectively.

The following kinetic equation is valid for the reaction in the presence of a nickel oxide–chromium oxide catalyst under the same conditions[100]:

$$r = kP_1^nP_{H_2}^m;\quad m = 1.5 - 1.2;\quad n = 0 - 0.5. \tag{13}$$

According to the authors[100], this corresponds to reaction via six slow stages involving consecutive addition of hydrogen and follows from a more general complex equation.

Thus the examples presented show that the kinetic models for the hydrogenation of organic compounds of different classes are distinguished by high specificity and a wide variety.

2. Isotope Exchange Reactions Involving Hydrocarbons

A kinetic model has been obtained[101-103] for isotope exchange reactions between hydrogen and deuterium in cyclohexane in the presence of nickel and platinum at low temperatures (up to 80°C). Previously, exact kinetic models for isotope exchange in hydrocarbons had been altogether absent from the literature. It was found that in the presence of nickel catalysts there is a possibility of two exchange mechanisms depending on the surface concentration of deuterium. In the presence of an excess of the latter, products with low degrees of substitution are formed, while in the presence of its deficiency mainly highly deuterated products are generated. The intermediate species responsible for isotope exchange in cyclohexane and benzene and for the hydrogenation of benzene were found to be different, i.e. the exchange in cyclohexane does not proceed via aromatic intermediates. In contrast to isotope exchange, the hydrogenation of benzene on nickel hardly occurs in the absence of hydrogen (deuterium) in the gas phase, i.e. the process requires the presence of weakly bound hydrogen (this can also be regarded as confirmation of the hydrogenation mechanism proposed above[4]). The rate of isotope exchange

$$C_6H_{12} + yD_2 = C_6H_{12-y}D_y + yHD,\quad y = 1, 2, \ldots, 12, \tag{14}$$

at low pressures and temperatures is described by the kinetic equation

$$r = k\frac{P_1P_{D_2}^{0.5}}{(k_1P_1 + k_2P_{D_2}^{0.5})^2}, \tag{15}$$

which holds both for the overall exchange and for the initial rates of formation of each product with different constants k. This is illustrated in Fig. 4, which shows that the rate of accumulation of each product constitutes a constant fraction of the rate of consumption of C_6H_{12}. Calculation of the isotope distribution in the products by a stochastic method yields values agreeing with experimental data only if simultaneous (and not consecutive) formation of all the substitution products in the initial stages of the processes is postulated (see Fig. 5).

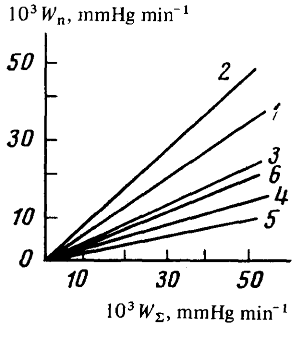

Figure 4. Dependence of the rates of accumulation W_n of different $[D_n]$ deuterocyclohexanes on the rate W_Σ of consumption of $[D_0]$ cyclohexane at 30°C in the presence of platinum: 1)–6) curves for the accumulation of $[D_1]$–$[D_6]$-cyclohexanes respectively.

The proposed scheme (Scheme 5) provides for the formation of all the products via the successive abstraction of hydrogen from the surface fragment on interaction with surface D atoms (for simplicity, it covers only the range y = 1–6). The formation of each product is described by the corresponding stoichiometric reaction pathway.

Scheme 5 also explains the different types of isotope distribution in the exchange products on nickel and platinum. This is due to the different ratios of the rates of reaction via pathway I and the remaining pathways, depending on the rates of stages 4 and 14.

Scheme 5*

Stage	Stoichiometric numbers of stages via different pathways					
	I	II	III	IV	V	VI
1. $D_2 = 2D_{ads}$	1	2	3	4	5	6
2. $C_6H_{12} = C_6H_{12ads}$	1	1	1	1	1	1
3. $C_6H_{12ads} + D_{ads} = C_6H_{11ads} + \underline{HD}$	1	1	1	1	1	1
4. $C_6H_{11ads} + D_{ads} = C_6H_{10ads} + \underline{HD}$	0	1	1	1	1	1
5. $C_6H_{10ads} + D_{ads} = C_6H_{10}D_{ads}$	0	1	1	1	1	1
6. $C_6H_{10}D_{ads} + D_{ads} = C_6H_9D_{ads} + \underline{HD}$	0	0	1	1	1	1
7. $C_6H_9D_{ads} + D_{ads} = C_6H_9D_{2ads}$	0	0	1	1	1	1
8. $C_6H_9D_{ads} + D_{ads} = C_6H_8D_{2ads} + \underline{HD}$	0	0	0	1	1	1
9. $C_6H_8D_{2ads} + D_{ads} = C_6H_8D_{3ads}$	0	0	0	1	1	1
10. $C_6H_8D_{3ads} + D_{ads} = C_6H_7D_{3ads} + \underline{HD}$	0	0	0	0	1	1
11. $C_6H_7D_{3ads} + D_{ads} = C_6H_7D_{4ads}$	0	0	0	0	1	1
12. $C_6H_7D_{4ads} + D_{ads} = C_6H_6D_{4ads} + \underline{HD}$	0	0	0	0	0	1
13. $C_6H_6D_{4ads} + D_{ads} = C_6H_6D_{5ads}$	0	0	0	0	0	1
14. $C_6H_{11ads} + D_{ads} = \underline{C_6H_{11}D}$	1	0	0	0	0	0
15. $C_6H_{10}D_{ads} + D_{ads} = \underline{C_6H_{10}D_2}$	0	1	0	0	0	0
16. $C_6H_9D_{2ads} + D_{ads} = \underline{C_6H_9D_3}$	0	0	1	0	0	0
17. $C_6H_8D_{3ads} + D_{ads} = \underline{C_6H_8D_4}$	0	0	0	1	0	0
18. $C_6H_7D_{4ads} + D_{ads} = \underline{C_6H_7D_5}$	0	0	0	0	1	0
19. $C_6H_6D_{5ads} + D_{ads} = \underline{C_6H_6D_6}$	0	0	0	0	0	1

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*Compounds evolved into the gas phase are underlined; stages 3–19 are assumed to be slow. Pathways VII–XII have been omitted for brevity as well as the subsequent stages 20, 21,...

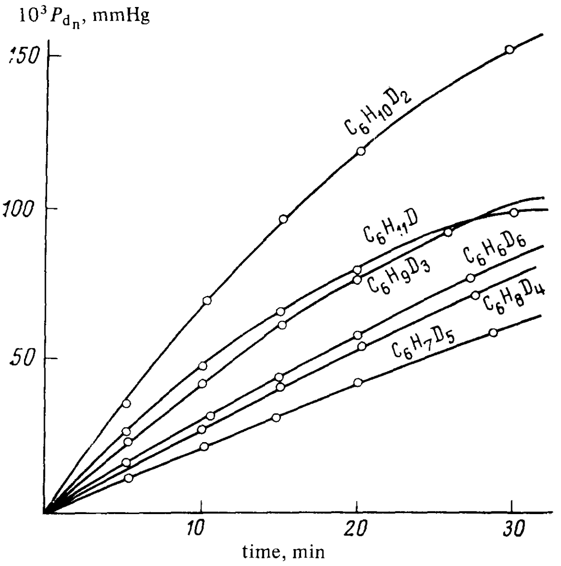


Figure 5. Time dependence of the distribution of isotopes in the products of the exchange between cyclohexane and deuterium at 30°C in the presence of nickel. The curves were calculated from the probable distribution based on the initial rates of formation of $[D_n]$cyclohexanes and the circles represent the experimental partial pressures of different $[D_n]$ cyclohexanes.

The model obtained actually relates for the first time the kinetics of the exchange in hydrocarbons to the nature of the isotope distribution and the mechanism of these multipathway reactions.

3. Dehydrogenation Reactions

The dehydrogenation of isopropyl alchol to acetone in the presence of nickel has been investigated in detail[104–106] in the region corresponding to the reversibility of the reaction (130–200°C):

$$iso\text{-}C_3H_7OH = CH_3COCH_3 + H_2. \quad (16)$$

Although this reaction has been frequently used by various investigators as a model, there were virtually no accurate kinetic literature data for this process. The kinetics of the reaction proved to be extremely unusual. The reaction is inhibited by one of the products (acetone), but is appreciably accelerated by the other (hydrogen), the rate of the process, measured in accordance with a single-parameter scheme[50], being proportional to the alcohol concentration. Fig. 6 compares the rates of dehydrogenation and isotope exchange in the alcohol and acetone.

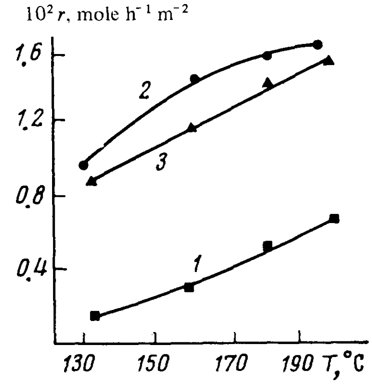


Figure 6. Temperature dependence of the rates of dehydrogenation of isopropyl alcohol (curve *1*) and the hydrogen–deuterium isotope exchange in isopropyl alcohol (curve *2*) and acetone (curve *3*) in the presence of nickel.

The rate of the overall isotope exchange in the alcohol exceeds approximately by a factor of three the rate of dehydrogenation, which is approximately the same as the rate of isotope exchange involving the hydrogen of the hydroxy-group. The nature of the isotope distribution in the exchange products (according to infrared and NMR spectra) and the results of the measurements of the kinetic isotope effects quoted below show that there is no intermediate enol rearrangement in this instance. Table 4 lists the kinetic isotope effects β for the replacement of protium by deuterium in the forward and reverse processes of the acetone hydrogenation reaction:

$$CH_3COCH_3 + H_2 = iso\text{-}C_3H_7OH; \quad (17)$$

here β is defined as the ratio of the rates of reactions involving compounds with the light (r_H) and heavy (r_D) isotopes under the same initial conditions and for the same composition of the reaction mixture:

$$\beta = r_H/r_D. \quad (18)$$

Table 4 shows that there is virtually no isotope effect in the substitution of protium by deuterium in the alkyl group of the alcohol, but it is appreciable for substitution in the hydroxy-group. This can be regarded as proof that the hydrogen of the hydroxy-group is involved in the slow stage (confirming the isotope exchange data) and that the adsorption and desorption stages are rapid.

Table 4. Kinetic isotope effects β in the dehydrogenation of isopropyl alcohol and the hydrogenation of acetone on nickel at 200°C.

Reaction	β	Reaction	β
$C_3H_7OH=C_3H_6O+H_2$ $C_3H_7OD=C_3H_6O+HD$	3.4	$C_3H_6O+H_2=C_3H_7OH$ $C_3D_6O+H_2=C_3D_6HOH$	1.0
$C_3H_7OH=C_3H_6O+H_2$ $C_3D_7OH=C_3D_6O+HD$	1.1	$C_3H_6O+H_2=C_3H_7OH$ $C_3H_6O+D_2=C_3H_6DOD$	0.8
$C_3H_7OH=C_3H_6O+H_2$ $C_3D_7OD=C_3D_6O+D_2$	4.3	$C_3H_6O+H_2=C_3H_7OH$ $C_3D_6O+D_2=C_3D_7OD$	0.8
		$C_3H_7OH=C_3H_6O+H_2$ (in excess of H_2) $C_3H_7OH=C_3H_6O+H_2$ (in excess of D_2)	3.5

The marked isotope effect in the replacement of the excess hydrogen by deuterium in the dehydrogenation of isopropyl alcohol confirms the involvement of hydrogen, in conformity with kinetic data. The observed low values of the isotope effects ($\beta < 1$) in reaction (17) are due to its specific features, which are analogous to those mentioned above for the hydrogenation of aromatic hydrocarbons. Comparison of the rate of reaction (16) with that of reaction (11) under the same conditions also demonstrated the impossibility of slow hydrogen desorption and adsorption stages.

The set of the above data corresponds to the following two-pathway scheme (Scheme 6), which provides for the simultaneous occurrence of the process via the slow abstraction of the hydrogen of the hydroxy-group directly from the adsorbed alcohol, which predominates at high concentrations of surface hydrogen:

Scheme 6

Stage	Stoichiometric numbers of the stages via different pathways	
	I	II
1. $H_2 = 2H_{ads}$	1	0
2. $CH_3CH(OH)CH_{3gas} = CH_3CH(OH)CH_{3ads}$	1	0
3. $CH_3CH(OH)CH_{3ads} = CH_3CH(O)CH_{3ads} + H_{ads}$(slow)	1	0
4. $CH_3CH(OH)CH_{3gas} + H_{ads} = CH_3CH(O)CH_{3ads} + H_2$(slow)	0	1
5. $CH_3CH(O)CH_{3ads} = CH_3COCH_{3ads} + H_{ads}$	1	1
6. $CH_3COCH_{3ads} = CH_3COCH_{3gas}$	1	1

With increase of the concentration of surface hydrogen, hydrogenation proceeds mainly as a result of the slow interaction of the gaseous alcohol with the surface hydrogen.

The kinetic equation giving the best (compared with all the other equations which have been tested) description of the experimental data follows from the scheme:

$$r = k\frac{P_1(1 + k^*P_{H_2}^{0,5})\,\gamma}{1 + k_1P_{ac} + k_2P_{ac}P_{H_2}^{0,5} + k_3P_{H_2}^{0,5}}, \tag{19}$$

where P_{ac} is the partial pressure of acetone and γ a correction for the influence of the reverse reaction (the unity in the denominator may not be neglected only for the description of the initial stage of the reaction for very low values of P_{ac}). Evidently the accelerating effect of hydrogen can be naturally accounted for within the framework of this scheme: it can be retained by the surface either during reduction or in the course of the reaction. A similar behaviour has been observed in the dehydrogenation of cyclohexane[107-109] and isopentenes[110] on palladium.

The above results also make it possible to characterise the kinetic model for the hydrogenation of acetone[111]. It corresponds to the reverse of Scheme 6 and the equation

$$r = k\frac{P_{ac}P_{H_2}(1 + k^*P_{H_2}^{0,5})\,\gamma}{1 + k_1P_{ac} + k_2P_{ac}P_{H_2}^{0,5} + k_3P_{H_2}^{0,5}}. \tag{20}$$

In the region corresponding to irreversibility, the rate of reaction (17) at lower temperatures (up to 90°C) is described by another equation according to Babkova et al.[112]:

$$r = k\frac{P_{ac}P_{H_2}}{(1 + k_1P_{ac} + k_2P_{ac}P_{H_2}^{0,5} + k_3P_{al})(1 + k'P_{H_2}^{0,5})}, \tag{21}$$

while in the presence of a copper catalyst it is described by the equation

$$r = k\frac{P_{ac}^2P_{H_2}}{(1 + k_1P_{ac} + k_2P_{ac}P_{H_2}^{0,5} + k_3P_{al})^2} \tag{22}$$

(P_{al} is the partial pressure of the alcohol).

Thus the complex kinetic investigation of the dehydrogenation of isopropyl alcohol in the presence of nickel in the region of reversibility made it possible to obtain concordant results and to elucidate the complex pattern of the reaction, which had been previously regarded as extremely simple. Conclusions concerning the characteristics of this process cannot, however, be extended to other dehydrogenation reactions. Thus quite different results were obtained[113-115] in a complex investigation of the selective dehydrogenation of cyclohexanol to cyclohexanone in the presence of a copper–magnesium catalyst at 210–270°C:

$$C_6H_{11}OH = C_6H_{10}O + H_2\ . \tag{23}$$

This shows that there are differences between the kinetic models. The rate of reaction (23) no longer depends on the concentration of hydrogen and there is no proportionality between the rate of the process and the concentration of the starting material, but inhibition by the ketone is also observed. The results of the measurements of the kinetic isotope effects for the forward and reverse processes are listed in Table 5.

Table 5. Kinetic isotope effects β in the dehydrogenation and hydrogenation of cyclohexanol at 240°C.

Reaction	β
$C_6H_{11}OH=C_6H_{10}O+H_2$ $C_6H_{11}OD=C_6H_{10}O+HD$ $C_6H_{11}OD=C_6H_9DO+H_2$	1.0
$C_6H_{11}OH=C_6H_{10}O+H_2$ (in excess of H_2) $C_6H_{11}OH=C_6H_{10}O+H_2$ (in excess of D_2)	1.0
$C_6H_{10}O+H_2=C_6H_{11}OH$ $C_6H_{10}O+D_2=C_6H_{10}DOD$	1.3

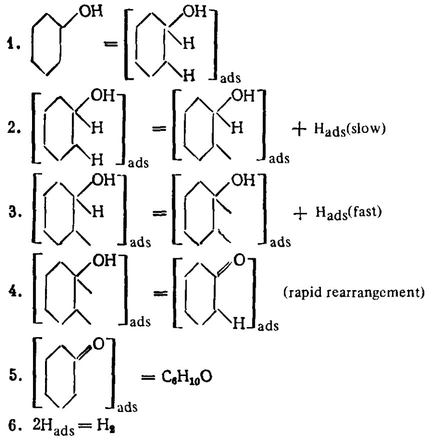
Evidently there is no isotope effect in the substitution of the hydrogen in the hydroxy-group and when the reaction is carried out in an atmosphere of deuterium, but it does operate in the reverse reaction. Experiments on isotope exchange showed that the rate of exchange of the hydroxyl hydrogen is higher than the rate of the reaction itself.

The rate of reaction (23) corresponds to Scheme 7 and the following kinetic equation:

$$r = k\frac{P_1\gamma}{(P_1 + k'P_{\text{ket}})^m}, \quad m = 0.5 - 0.6, \tag{24}$$

where P_{ket} is the partial pressure of cyclohexanone. Scheme 7 presupposes the occurrence of the reaction via the slow abstraction of β-hydrogen and rapid enol rearrangement.

Scheme 7



Thus a change in the structure of the molecule and the use of a different metallic catalyst have a significant influence on the form and properties of the kinetic model, while the general character of the reaction remains the same. The kinetic models for the dehydrogenation of hydrocarbons have a completely different form[116-118]. This shows yet again that dehydrogenation processes cannot be embraced by a general kinetic model, as suggested previously by some workers.

4. Extensive Oxidation of Microadmixtures of Organic Substances

These reactions were investigated in relation to the oxidation of microadmixtures of n-pentane, benzene, and their mixtures[119,120] in the presence of an aluminium-platinum [alumina-platinum?] catalyst and platinum foil at 100–350°C over a wide range of conditions. The rate of extensive oxidation of benzene is expressed by the equation

$$r = \frac{kP_1P_{O_2}^{0{,}5}}{(1 + k_1P_1 + k_2P_1P_{O_2}^{0{,}5} + k_3P_{H_2O}P_{O_2}^{-0{,}5})^2}; \tag{25}$$

at fairly high oxygen concentrations ($P_{O_2} \geqslant 0.1$ atm), we have

$$r = kP_1/(1 + k'P_1)^2. \tag{26}$$

At 130°C and above, a heterogeneous-homogeneous process mechanism operates to some extent (this was demonstrated by the inhibiting effect of the packing in a reactor with a vibrofluidised catalyst bed[121] and directly by the method involving separate calorimetric measurements[122]), which leads to the appearance of additional terms in Eqns. (25) and (26). This is a fairly rare instance; the homogeneous propagation of the oxidation reactions of organic compounds (which is in general not observed very frequently) usually occurs only at 400–600°C[123,124]. Above 240°C, the reaction passes to the external-diffusion region. When benzene is replaced by deuterobenzene, there is no kinetic isotope effect, so that the slow stages of the process apparently do not entail the dissociation of C–H bonds. The mechanism of the process presupposes its simultaneous occurrence via four independent pathways: the purely heterogeneous pathway (via successive oxidative cracking on the surface of platinum coated with oxygen with slow stages involving the conversion of aromatic bonds into ordinary bonds), the heterogeneous-homogeneous pathway (with transfer of the intermediate oxygen complexes of benzene into the gas phase and their subsequent interaction with molecular oxygen) and two "empty" pathways involving the deactivation of radical-like compounds in the gas phase.

The characteristics of the extensive oxidation of n-pentane are quite different; there is no homogeneous propagation of the reaction and the kinetic isotope effects show that the slow stages involve the dissociation of C–H bonds, the rate of the process being described by the equation

$$r = kP_1, \tag{27}$$

which corresponds to a scheme presupposing slow dissociative adsorption of pentane on the oxidised surface of platinum.

When both hydrocarbons are oxidised simultaneously, pentane does not affect the oxidation of benzene; at low concentrations, benzene does not affect the oxidation of pentane up to a certain critical concentration beyond which benzene causes a sharp inhibition of the pentane oxidation reaction. The rate of oxidation of pentane in the presence of benzene is characterised by the equation

$$r = k\frac{P_1}{(1 + k'P_{C_6H_6})^2}, \tag{28}$$

corresponding to kinetic models involving separate oxidation processes.

The above examples show that accurate complex investigations lead to exceptionally varied and specific kinetic models for different classes of reactions and catalysts.

IV. NON-STEADY-STATE KINETIC MODELS

The kinetic models discussed above characterise steady-state or quasi-steady-state reactions. The concentrations of the intermediates formed and decomposed during the process then remain constant under specified conditions, corresponding to the given constant concentrations of the reactants, and when the latter are altered, there is sufficient time for new concentrations of the intermediates corresponding to them to be established. Steady-state conditions can frequently break down, so that the catalytic reactions proceed as non-steady-state processes. Such breakdown is caused, particularly, by the activation of the catalyst in the initial stages of the reactions, by the gradual blocking of the surface by side products, by the influence of the reaction system, by the changes associated with transitions to other conditions, and by other factors causing oscillations or steady alterations in the activity of the catalysts[125-127].

Analysis demonstrates the possibility of the occurrence of more than one steady state of the process in the kinetic region, depending on its mechanism and the nature of the kinetic model[128-132]. The necessary condition for this is the presence of stages involving interaction between different intermediates[128-132,164-166]. A multiplicity of steady states has been observed experimentally, for example, in the reaction of carbon monoxide with hydrogen in the presence of nickel[141].

The attainment of a steady state requires a certain relaxation time of the rate of reaction[126,133,167,168]. In conformity with Frank-Kamenetskii's conditions[169], it must be much shorter than the reaction time and must depend on the conditions of the process, its mechanism, and the ratios of the rates in different stages (Belousov[170] refers to the relaxation time as the duration of the intrinsically non-steady state). Temkin[126,167,168] showed that the relaxation time constitutes in the general case a fraction of the "reaction turnover time", which is the reciprocal of the "reaction turnover number"[41] (i.e. the number of molecules which have reacted per unit time referred to the number of active sites on the catalyst surface).

The relaxation time characterises the time required for the attainment of the steady state, determined by the specific features of the multistage nature of the process and its mechanism, but not by other influences caused by the effect of the reaction system on the catalyst and secondary factors. Relaxation in consequence of such "secondary influences"[126,168] may be much more prolonged than the reaction itself and the process as a whole then takes place under non-steady-state conditions. Such a situation arises, for example, in the oxidation of ethylene in the presence of silver[171] owing to the modifying effect of the oxygen penetrating into the surface layer of the catalyst.

Experimental studies on processes under non-steady-state conditions, both in order to determine the relaxation time as a function of various factors and to elucidate other characteristics, can therefore serve as an effective means for devising kinetic models required for a more complete understanding of catalytic processes. Certain approaches of this kind have been described in the literature, for example, in Refs. 42, 43, 133–139, and 172–175. Thus the determination of the ignition limits in the synthesis of alcohols on transition of the latter from the kinetic region to the external-diffusion region has been used to describe the rate of this process[133]. The study of decay phenomena as a function of various factors in the transition of the ammonia oxidation reaction on a non-platinum catalyst from the external-diffusion to the kinetic region made it possible to derive a kinetic equation for the reaction[139]. Non-steady-state effects in the ammonia and sulphur dioxide oxidation reactions have been investigated[174,175] by the electrothermographic method. The parameters of the non-steady-state kinetic models for the oxidation of carbon monoxide on platinum and lanthanum trioxide have been determined and the models have been analysed[128,176,177]. The kinetics of the oxidation of hydrogen in the presence of nickel under the conditions of stable auto-oscillations of the system, having a chemical mechanism, have been investigated by Slin'ko and coworkers[142,178,179].

Non-steady-state kinetic models have also been obtained for the hydrochlorination of acetylene[143], the oxidation of propene, and its oxidative ammonolysis[144]. For a model of this kind, Gel'bshtein and coworkers[144] reported to the earlier idea[180] of a surface "reaction layer" of the catalyst, where oxygen ionises and is transferred from centres of one type to those of another. They believe[144] that the thickness of this layer determines the occurrence of the process under particular conditions. When the layer is thin, the characteristics of the steady-state and non-steady-state course of the reaction are the same. Many non-steady-state kinetic models have been devised for the description of the dehydrogenation of hydrocarbons, taking into account the blocking of the catalyst by coke[116,117,145-147,181-183] (although not all such models have been adequately justified). The earlier models for the dehydrogenation of hydrocarbons containing four carbon atoms in the presence of alumina–chromium oxide catalysts have been reviewed[184].

A kinetic model (unsupported by multistage mechanisms), taking into account the rates of conversion of butane into butenes (r_1) and of butenes into butadiene (r_2), of the cracking of butane (r_3), and of coke formation from both hydrocarbons (r_4 and r_5) has been proposed for the single-stage dehydrogenation of butane in the presence of an alumina–chromium oxide catalyst in the temperature range 570–630°C [145]:

$$r_1 = k_1(1 - c/c_{\max})P_1\gamma/M^2, \tag{29}$$

$$r_2 = k_2(1 - c/c_{\max})^2 P_{C_4H_8}\gamma/M^2, \tag{30}$$

$$r_3 = k_3(1 - c/c_{\max})P_1/M, \tag{31}$$

$$r_4 = k_4P_{C_4H_8}/M^2, \tag{32}$$

$$r_5 = k_5P_{C_4H_6}/M^2, \tag{33}$$

where M depends on the concentrations of all the reactants and the rate of the main reactions depends on the area of the coke-free surface (c and $c_{\max}$ are the concentration of coke at any instant and the concentration corresponding to monolayer coverage).

The dependence of the rate of the process on the amount of coke and the influence of the oxygen concentration ω in the surface layer of the catalyst, which varies owing to the slow diffusion of oxygen during preliminary treatment and during the reaction itself, have been refined[148]:

$$r_1 = k_1\omega\,e^{-uc}P_1\gamma/(1 + k'P_1)^2, \tag{34}$$

$$r_3 = k_3P_1, \tag{35}$$

$$r_4 = k_4P_{C_4H_8}, \tag{36}$$

$$r_5 = k_5\omega P_{C_4H_8}/P_{H_2}. \tag{37}$$

Under the experimental conditions (535–585°C), the conversion of butenes into butadiene is reversible and the changes in ω are defined by equations for diffusion in a solid. A similar exponential dependence of the rate of the process on coke concentration characterises the kinetic models for the dehydrogenation of butane and isopentane in the presence of another alumina–chromium oxide catalyst[147,148]. A kinetic equation analogous to Eqn. (29) with $M = 1$, to which a linear decrease of the rate of reaction with increasing coke concentration corresponds, is valid for the dehydrogenation of isobutane to isobutene in the presence of an alumina–chromium oxide catalyst[146].

A study of the kinetics of the dehydrogenation of isopentenes to isoprene in the presence of a zinc–chromium [zinc oxide–chromium oxide?] catalyst[116-118,186] at 540 to

620°C using ^{14}C and deuterium led to the derivation of the equation

$$r = k^{*} \frac{P_1\gamma}{(P_1 + k'P_{C_5H_8})^{0,5}}, \tag{38}$$

where the constant k^* depends in the general case on the change in the free energy of the system ΔG_X for the given degree of conversion x, which affects the free energy of the catalyst surface (taken into account by the factor a), and also on the amount of coke:

$$k^{*} = k\,(1 - lc/c_{\max})\,e^{-a\Delta G_x/RT} \tag{39}$$

(where l is a variable multiplier close to zero, reaching unity for $c = c_{\max}$) and $a \simeq 1$. This equation corresponds to the scheme taking into account the slow abstraction of hydrogen from the most reactive isomer (2-methylbut-2-ene) accompanied by the attainment of isomerisation equilibrium. The changes in free energy have a marked influence on the rate of the process, causing considerable alterations in the latter for a small increase in the degree of conversion.

The same reaction in the presence of a nickel–phosphate catalyst is described by a more complex kinetic model[181-183] characterising the rate of dehydrogenation (r_1), the formation of light hydrocarbons from isopentenes (r_2), and coke formation (r_3) in the temperature range 580–680°C and also the rate of regeneration of the catalyst (r_6):

$$r_1 = k_1 \frac{P_1\gamma}{c^{2/3} + k'P_{C_5H_8}}, \tag{40}$$

$$r_2 = k_2 \frac{P_1}{c^{2/3} + k'P_{C_5H_8}}, \tag{41}$$

$$r_3 = \frac{k_3P_1 + k_3^{*}P_{C_5H_8}}{c^{2/3} + k'P_{C_5H_8}} + \frac{k_3'P_1 + k_3''P_{C_5H_8}}{(c^{2/3} + k'P_{C_5H_8})^{0,5}}\,c^{2/3}\,e^{-\alpha c}, \tag{42}$$

$$r_6 = k_6 \frac{P_{O_2}c^{2/3}}{P_{O_2} + k_6'c^{2/3}}. \tag{43}$$

These equations follow from the general multistage mechanism (i.e. are not empirical), which presupposes that the reaction proceeds via reversible isomerisation stages, slow successive elimination of hydrogen from the adsorbed isopentenes, their cleavage, and coke formation on the free surface as well as the surface already occupied by coke. The experimental kinetic isotope effects obtained[183] agree with this mechanism.

The kinetics of cracking reactions under non-steady-state conditions, due to the decrease of the activity of the catalyst caused by the blocking of the active surface sites, have been considered by Wojciechowski (see his review[187]) on the basis of ideas which he developed. These refer only to the simplest instances of previously postulated mechanisms and lead to time-dependent non-autonomous models. The requirement that the model be independent of time is extremely important for its practical employment[140]. Models describing the decrease of activity have also been discussed in a number of other studies (see, for example, Refs. 188–192). Non-steady-state changes may arise as a consequence of the rearrangement of the active sites on the catalyst surface during the reaction and the formation of surface phases. The kinetics of such processes have been examined in a general form[193].

The formal kinetic descriptions of the reaction under steady- and non-steady-state conditions can naturally be significantly different. Certain simplest cases of such changes and transitions from one set of conditions to another have been discussed[170,194]. However, apart from the intrinsic non-steady state (see above), only the non-steady chemical state, in which the chemical composition of the catalyst is brought into correspondence with that of the gas phase after the attainment of adsorption equilibrium, has been examined in these investigations. This limitation rules out a general approach to this problem.

If the processes corresponding to the attainment of a steady state during the relaxation of the rate of reaction are considered for a fixed number of active sites on the catalyst surface, all the "extraneous" non-steady-state processes caused by the influence of some other factors (the influence of the reaction system, etc.) are as a rule associated with changes in the number or quality of active regions. The mechanism of such changes is in most cases insufficiently clear and a mathematical description taking them into account in kinetic models is much more complex than the description of the steady-state cases. A further development of experimental techniques and approaches to the interpretation and description of the results is therefore necessary for the investigation of the kinetics of non-steady-state processes. This is significant also owing to the practical importance of non-steady-state conditions, particular examples of which may arise in processes with a pseudofluodised catalyst bed or with a moving bed. The possibility of non-steady-state changes and the effectiveness of such, perhaps even brief non-steady-state conditions, which have proved to be more suitable than steady-state conditions[127,128], result in an extremely urgent need for studies designed to obtain and interpret non-steady-state kinetic models.

At the same time, since the bulk of catalytic industrial processes are nowadays carried out under steady-state conditions, further research on processes under steady-state conditions and establishment of steady-state kinetic models are equally necessary. Both types of research should naturally supplement one another, clearly under conditions where non-steady-state effects are real, currently important, and useful. The search for such non-steady-state effects can also prove extremely useful, which in no way diminishes the importance and the amount of information derivable from steady-state models which can lead to the process mechanism by a more direct and productive procedure.

The problems of non-steady-state kinetics may be the subject of a separate review.

V. OPTIMUM KINETIC MODELS

Each kinetic model must reflect real specific properties of the reaction–catalyst system investigated under the given conditions. If the kinetic equation for the reaction via one of the pathways is considered in a general form, it can be represented[48] as a product of the initial velocity r_0 ("reaction level") and a function of the degree of conversion $\Phi(x)$ (normalised to unity), which determines the form of the kinetic model:

$$r = r_0\Phi(x). \tag{44}$$

The level r_0 depends on the initial conditions, the amount of the catalyst, its activity and adsorption capacity, and the specific form of the kinetic equation, to which the function $\Phi(x)$ is extremely sensitive (see Fig. 7). Fig. 7 shows that changes in r relative to r_0, which are determined by the changes in $\Phi(x)$ during the process, from $x = 0$ to $x \simeq 1$, will be smallest for a zero-order reaction.

For other kinetic relations, there is a steady decrease of the reaction rate, which is more marked for higher-order reactions and when the reaction is strongly inhibited by its products. Relations with extrema are also possible, but these need not be discussed here, since they do not alter our conclusions.

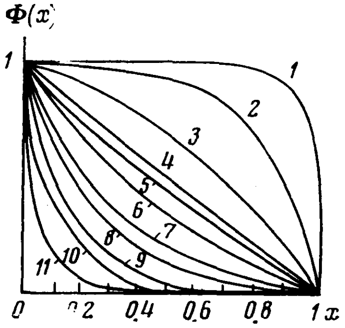


Figure 7. Dependence of the form of $\Phi(x)$ on the degree of conversion for different kinetic equations $r = kP_1^n/P_{prod}^m$: 1) $m = 0$, $n = 0$; 2) $n = 0.3$; 3) $n = 0.5$; 4) $n = 1$; 5) $n = 1.5$; 6) $n = 2$; 7) $n = 3$; 8) $m = n = 0.5$; 9) $m = 0.5$, $n = 2$; 10) $n = 0.5$, $m = 1$; 11) $n = m = 1$.

Thus the form of the kinetic model, specified by the kinetic equation, describes the nature of the changes in the rate of the process, throughout its course, under steady-state conditions. From this standpoint, one may speak of the optimum form of the kinetic model, reflecting the most convenient type of changes in the rate of the reaction throughout the latter. Since high or the maximum possible conversions (for the given selectivity) are of greatest interest for practical use, the minimum decrease of the rate of reaction compared with its initial value as the degree of conversion increases is the most convenient. The form of the kinetic model characterising the smallest changes in the reaction rate with increasing degree of conversion, other conditions being equal, may be regarded as the optimum form. It is clear from the foregoing that the form describing a zero-order reaction or other similar relations, in which the decrease of the rate of reaction during the process is a minimum compared with the relations corresponding to other kinetic equations possible for the given system, is the optimum form[149].

However, the fact that the model has the optimum form does not yet show that the model as a whole is optimum, which depends on the superposition of various factors. If we again restrict ourselves to a single stoichiometric reaction pathway, then, for the specified activity of the catalyst and the optimum form of the kinetic model, the latter is optimum as a whole when the level r_0 is higher than that corresponding to other kinetic models.

Thus the model which adequately describes the changes in the reaction rate during the process, which are the smallest possible compared with the initial level r_0 (r_0 being greater than other possible values obtained for other models under the specified conditions and for the specified catalyst activity), may be regarded as the optimum model. The optimum properties treated in this way depend on the internal characteristics of the process, which determine the given kinetic model. Consequently one may be dealing with kinetically optimum reaction mechanisms from which follow optimum kinetic models. The kinetically optimum reaction mechanism (which depends on the reaction conditions and the catalyst properties) will then be one ensuring that the optimum kinetic model arises from it, i.e. the most convenient form of the model and the most convenient initial process velocity. Hence it follows that, in selecting the catalyst, it is useful to take into account whether or not it can ensure a rate of the process whose value and the changes in the latter correspond to the optimum or nearly optimum kinetic model.

Analysis of the kinetic relations arising from various possible multistage process mechanisms and the relative rates of the stages may indicate which models are optimum or nearly optimum for the specified activation energy under the given conditions, together with approximate estimates of the rate constants for the elementary stages by the transition state method. Such analysis of the optimum properties of the models may constitute one of the stages in the selection of catalysts accompanied by the consideration of the possible properties and composition which would ensure the required kinetically optimum mechanism.

An estimate[149] has shown that the most convenient form of the model, i.e. the most nearly zero-order reaction, corresponds in most instances also to the highest level r_0 for the specified activation energy, provided that the reaction proceeds via slow stages involving surface interaction or desorption (the activation entropy is zero or higher). The initial velocities for different forms of the models proved to be extremely different and the replacement of a zero-order equation by other equations alters the level r_0 so much that the influence of the decrease in the latter on the rate of reaction may be compensated only by an improbably large decrease of activation energy.

Table 6. The degree of approach to an optimum by the kinetic models for certain reactions[149].

Reaction	Model characteristics	Remarks
Isomerisation of cyclohexene to methylcyclopentane on CaY zeolite (0.5% Pt); 268–320°C; 13–17 atm (Ref.150)	Zero-order equation corresponding to rapid formation of C_6H_{10ads} and its slow conversion into $C_5H_9CH_{3ads}$	Nearly optimum model
Hydrogenation of benzene on nickel; 90–150°C; 1 atm (Refs. 74,100)	The observed equation $r = kP_{H_2}^{0.5}$ is closer to a zero-order equation than other possible expressions; it corresponds to the slow conversion of C_6H_{6ads} into C_6H_{7ads} (Ref.151)	Model closer to an optimum under the given conditions than other models
Oxidation of hydrogen on oxide catalysts (Sn, Mo, W, Cd, Mn, V, Co, Cr, Cu, and Ni oxides) (Refs.152,153)	The rate of the process is described by a first-order equation with respect to hydrogen and corresponds to an oxidation-reduction mechanism or other multistage mechanisms.	Model closer to an optimum than the model corresponding to single-stage mechanisms.

Table 6 presents the results of the analysis[149] of certain simple models as regards their optimum properties, using literature data[74,100,150–153].

The kinetic models listed in Table 6 may be closer to the optimum model than others for the same reaction under different conditions or in the presence of other catalysts. For example[149], if the isomerisation of cyclohexene proceeded in a single stage (i.e. in accordance with another model), its rate would be described by a first-order equation (and not a zero-order equation as in the model described above), with values of r smaller by several orders of magnitude (for the same experimental activation energy and under the same conditions). Consequently the model with the optimum form also corresponds to the highest initial velocity of the reaction.

It has been shown for the hydrogenation of benzene[48,74] that the rate of the process under the given conditions, characterised by the model in Table 6, is higher than when the process is described by other kinetic equations: $r = kP_1P_{H_2}$ or $r = kP_1^{0.5}P_{H_2}^3$.

Analysis[149] also leads to the conclusion that the rate of the reaction corresponding, for example, to the Parravano mechanism[195] (the slow stage involves the adsorption of hydrogen and its subsequent rapid interaction with benzene in the gas phase) would be described by a more complex kinetic relation and would be lower approximately by 8 orders of magnitude than for the model in Table 6. If Kagan's mechanism[96] were valid (slow formation of cyclohexadiene with subsequent rapid disproportionation), the kinetic equation for such a model would be complex with a sharper decrease of the rate of reaction compared with the initial value and the rates r under the specified conditions for the given activation energy would be in order of magnitude lower than for the model in Table 6[149].

According to the results of Goncharuk and Golodets[152], the rate of oxidation of hydrogen in the presence of tungsten trioxide under conditions such that a first-order equation (which is closer to the optimum expression than the other observed kinetic relations) does not hold, proves to be an order of magnitude lower than in the presence of the same catalyst when the equation does hold. Comparison of the activation entropies for oxidation reactions carried out by Boreskov[154] also showed that the entropy is much higher for the oxidation-reduction mechanism than for a single-stage reaction. The form of the kinetic model is also much less favourable[149] for the single-stage mechanism. According to Popovskii et al.[153], the rate of oxidation of hydrogen in the presence of chromium trioxide at 226°C, where a kinetic equation with a fractional order holds ($r = k_0e^{-20\,000/\mathrm{RT}}P_{H_2}^{0.6}$), is approximately the same as in the presence of V_2O_5 at a much higher temperature (440°C), where a first-order kinetic equation $r = k_0e^{-21\,000/\mathrm{RT}}P_{H_2}$ is valid (evidently the activation energies are similar in the two cases and cannot be the cause of the discrepancy between the values of r at comparable temperatures). Consequently, for the form of the kinetic model closer to the optimum, which obtains in the presence of chromium oxide, the initial reaction rate is much higher than in the presence of V_2O_5, where the form of the model is further removed from the optimum.

The turnover number of the reaction[41] can serve as a quantitative characteristic of its initial level, because it refers, as a rule, to a degree of conversion of zero. Maatman[197] calculated the turnover numbers for different reactions and catalysts assuming in many instances that the reactions proceed in accordance with a zero-order equation and an activation entropy close to zero. If his values were sufficiently well-founded, the greatest turnover number would correspond precisely to the optimum model. Thus, according to his calculations[197], the turnover number for the cracking of cumene on a "decationated" zeolite is higher by many orders of magnitude than on an aluminosilicate catalyst. Thus Maatman's results show that, despite the optimum form of the kinetic models in the two instances, they differ sharply as regards the level of the reaction and therefore the first model must be regarded as optimum. Unfortunately, Maatman's calculations are not based on accurate kinetic data and accurate information about the reaction mechanism.

The above examples demonstrate the usefulness of the analysis of the optimum properties of kinetic models. In the selection of catalysts it is therefore useful to carry out an analysis in order to determine which kinetic models could describe the reaction in the presence of the selected catalyst and which additives (if the possible mechanism of their action is considered) could lead to other models closer to the optimum. Naturally such an approach is extremely simplified and one-sided, but, when the appropriate information is available, it can be very useful. Kol'tsov, Beskov, and the present author[196] considered in general terms the optimum process conditions which may be predicted from the form of kinetic models (references to preceding communications are given in this paper).

VI. KINETIC MODELS AND REACTION SELECTIVITIES

The selectivity is one of the most important kinetic factors characterising the course of complex reactions and determining their practical employment. It can be expressed as the ratio of the sum of the reaction rates via pathways leading to the formation of the desired product to the sum of the rates of all the transformation of the initial substances under identical conditions[156] ("differential selectivity"[155]). This ratio characterises the true process selectivity. Since the desired product can undergo secondary transformations, it is necessary to consider the apparent selectivity[156,157] taking into account the rate of accumulation of the desired product W_j as the algebraic sum of the rates of reaction via all the pathways leading to its formation and decomposition (for the given composition of the reaction mixture):

$$\begin{gathered} S = W_j/W_1, \\ P_1^0,\ P_2^0,\ \ldots = \text{const},\ x = \text{const};\ T = \text{const}, \end{gathered} \tag{45}$$

where W_1 is the overall rate of the transformations of the starting material. This expression for a reaction in a gradient-free system[1] is identical with the expression for the integral selectivity—the ratio of the amount of the desired product to the overall amount of all the products.

The changes in selectivity during the process evidently depend on its nature, which is determined by the properties of the kinetic model and the rates of reaction via different pathways. These changes, caused by the form of the dependence of the reaction rates on the degree of conversion which follows from the given kinetic model, may be different for different selectivities.

Such instances reflect a parallel process mechanism (where the desired product does not undergo further transformations on being separated from the catalyst), or a consecutive mechanism (the desired product is partly returned to the surface and is converted into side products), or a parallel-consecutive mechanism (a combination of the first two mechanisms). The expression for the selectivity covering these instances follows from Eqns. (44) and (45)[156,157,198]:

$$S = \left(1 - \eta\frac{\Phi_{\mathrm{III}}(x_{\mathrm{III}})}{\Phi_{\mathrm{I}}(x_{\mathrm{I}})}\right) \Bigg/ \left(1 + \alpha\frac{\Phi_{\mathrm{II}}(x_{\mathrm{II}})}{\Phi_{\mathrm{I}}(x_{\mathrm{I}})}\right). \tag{46}$$

Here subscripts I, II, and III indicate the pathways leading to the formation of the desired product and the parallel and consecutive formation of side products, $\alpha = r_0^{\mathrm{II}}/r_0^{\mathrm{I}} = \text{const}$.

(i.e. the initial reaction rates via parallel pathways do not vary during the process), but $\eta = r_0^{\mathrm{III}}/r_0^{\mathrm{I}} \neq \mathrm{const.}$ (i.e. the initial rate of reaction via pathway III changes continuously owing to the changes in the concentration of the desired product); $\eta = 0$ for the parallel mechanism and $\alpha = 0$ for the consecutive mechanism.

Eqn. (46) indicates a direct relation between the form of the kinetic model and the changes in selectivity. From this it follows that the constancy of the selectivity during the process is possible only under certain conditions: (a) when the reaction proceeds in accordance with a zero-order equation via all the pathways (an unlikely case); (b) $\alpha \ll 1$ and $\eta \ll 1$ (i.e. reaction via the main pathway I predominates throughout the process) whereupon $S \simeq 1$; (c) when the process proceeds via a parallel mechanism, the kinetic equations for both pathways are identical, and there is no inhibition by the products.

Consequently the independence of the selectivity of the degree of conversion over a fairly wide range of the latter when S is appreciably different from unity may correspond only to a fully defined type of the kinetic model for the process. This is illustrated, for example, by the isotope exchange reaction in cyclohexane, discussed above, when its rates via all the parallel pathways are described by identical kinetic equations (Fig. 4). The properties of the kinetic model, characterised by identical kinetic equations in the absence of inhibition of the reaction via all the pathways by its products, determine the constancy of the ratios of the reaction rates via these pathways throughout the process. The latter is equivalent to the constancy of reaction selectivity for variable degrees of conversion [this should in its turn indicate the parallel formation of all the products, confirming the multistage mechanism (5)]. Evidently, the selectivity in the given instance serves as an additional factor whereby one can test and confirm the proposed kinetic model, which determines the observed characteristics of the selectivity (see also Butovskii et al.[182]).

An increase of selectivity during the processes is possible if the reaction via the required pathway is inhibited by its products to a lesser extent than via the remaining parallel pathways (for example, in the oxidation of cyclopentadiene[158]) or when the desired product is formed via several pathways and the formation of other products is inhibited by the initial substance. The latter case is observed in the oxidative ammonolysis of xylenes[159]. For example, isophthalonitrile is formed in this reaction from *m*-xylene in accordance with a second-order equation and the formation of extensive oxidation products is inhibited by the initial xylene, such products being obtained only from the initial xylene and the intermediate tolunitrile but not from the desired product (isophthalonitrile). One may therefore expect an increase of selectivity with increasing degree of conversion; this is in fact observed, which indicates the validity of the chosen kinetic model. Eqn.(46) shows that in other instances the selectivity should decrease during the process in conformity with numerous data[157].

Thus the properties of kinetic models determine to a significant extent the magnitude and nature of the changes in selectivity, which may be used in the analysis of kinetic relations.

Analysis of the changes in selectivity for processes described by different kinetic power equations is described in a book[199]. Golodets and coworkers[200-202] obtained and analysed expressions for the selectivity corresponding to the kinetic equations for certain oxidation reactions. The expressions can also be used in the analysis of kinetic models.

VII. ESTIMATION OF THE ACTIVITIES OF CATALYSTS OF COMPLEX REACTIONS

The problems associated with the tests, estimations, and comparison of the activities of catalysts are purely kinetic, since the only objective criterion of catalytic activity is the rate of reaction under the specified conditions and for the given composition of the reaction mixture[155,156,160,161]. For complex processes occurring via different pathways, the rate of accumulation of the desired product[156], i.e. the algebraic sum of the rates of reaction via independent pathways leading to its formation and decomposition, can serve as a criterion of the activity of catalysts. Since the rate of reaction depends on the degree of conversion, information about the rates of accumulation of the desired product for different compositions of the reaction mixture and for different conversions at the limits of the ranges of variation of the specified process parameters is desirable if sufficiently complete characteristics of the catalytic activity are to be obtained.

For objective tests and comparison of catalytic activities, exact measurements of the rate of reaction in the presence of distorting transport effects (and when internal-diffusion inhibition cannot be eliminated also with allowance for the latter) are necessary. It is useful to carry out such tests in gradient-free apparatus. The results of the tests can be expressed by "conversion curves"[48] relating the rate of reaction to the degree of conversion under specified initial process conditions.

The problem of tests of the activity of catalysts used under non-steady-state conditions is naturally more complicated. It requires the determination of the relation between the activity of the catalyst and various factors, particularly the duration of the continuous process, which depends in its turn on the concentration of impurities, the changes in the state of the catalyst as a consequence of the influence of the reaction system, etc. In this case it may be useful to combine tests in gradient-free apparatus with non-steady-state methods providing for the simultaneous monitoring of the state of the catalyst and the changes in the latter. Such methods are urgently required in preliminary studies and subsequent development [of the process?].

Exact tests and an objective estimate of catalytic activity and selectivity are evidently by no means easy and for complex reaction systems, for example for petroleum processing reactions, the problem is far from solution, although there are publications in this field[162,163]. However, despite the difficulties which must be faced in its solution (particularly in the case of tests of catalysts in non-steady-state processes), the magnitude of the problem is in no way comparable to the problem of devising kinetic models which requires a much greater expenditure of time and effort.

Despite this, further development of new effective and rapid methods for the testing of catalysts of complex reactions and the estimation of their activity and selectivity constitutes one of the most important problems of chemical kinetics in heterogeneous catalysis.

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In conclusion one may note that further development of the theory and practice of heterogeneous catalysis will depend to a considerable extent on the strength of its kinetic foundation. It is based on informative kinetic models for various catalytic processes. The valuable information which can be derived from these models should help in understanding the essential features of catalytic activity and should extend the practical employment of catalysis. In order to set up such models, it is useful to carry out complex kinetic investigations. Although the methods for devising kinetic models and their analysis have been adequately developed, they require new approaches and further expansion, particularly for non-steady-state processes. The possibilities arising from complete, reliable, exact, and well-founded kinetic models, some of which were described above, make the task of their formulation and general treatment exceptionally important and necessary.

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Oxidation-reduction Reactions of Free Radicals

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The results of experimental studies on the oxidation-reduction reactions of free radicals with organic donors and acceptors and transition metal compounds involving one-electron transfer are surveyed. Attention is concentrated on studies performed in recent years (up to 1976 inclusive) in which the reactions of short-lived radicals have been investigated by pulse radiolysis, stopped flow, ESR, polarographic, and flash photolysis methods. The relation between the structures and reactivities of radicals in such porcesses and the methods for the measurement of their oxidation-reduction potentials are examined. Data on the formation of complexes of radicals with metal compounds are presented.

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I. INTRODUCTION

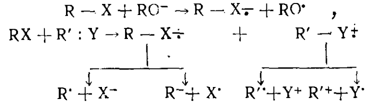
Various radical reactions proceed in the presence of metal compounds and electron donors and acceptors. Many of them are of biological importance and take place in living organisms. Free radicals, which have a high electron affinity, behave in most cases as vigorous oxidants. However, there are data suggesting that free radicals are in a certain sense amphoteric, i.e. are capable both of capturing an electron to form the carbanion and of transferring the unpaired electron to a sufficiently strong acceptor with formation of the corresponding cation[1]. Radical-ions are strongly involved in oxidation-reduction reactions, behaving as electron donors or acceptors (reactions with organic halides, initiation of polymerisation, exchange reactions, etc.).

There has been an increase of interest in recent years in the oxidation-reduction and complex-formation reactions of radicals in connection with the elucidation of the detailed mechanisms and kinetics of many homogeneous-catalytic processes, particularly liquid-phase oxidation reactions†. Emanuel' and coworkers[2-5] demonstrated the inhibiting or catalytic (depending on the conditions) effect of transition metal compounds on liquid-phase chain oxidation reactions of hydrocarbons.

The interaction of radicals with metal compounds, which are oxidation-reduction or complex-formation processes, has been postulated for a fairly long time. However, only in the last five-ten years numerous experimental data, demonstrating convincingly the occurrence of radical reactions of this class, have been obtained as a consequence of the development of the relevant experimental techniques. This review deals with the results of studies on oxidation-reduction and complex-formation reactions of radicals obtained mainly by the direct recording of the structure of the radicals and of the rates of their destruction. Attention has been concentrated on the reactions of short-lived radicals in the liquid phase.

II. ONE-ELECTRON OXIDATION (REDUCTION) OF RADICALS BY ORGANIC COMPOUNDS

It has been suggested that electron transfer is the elementary step in many organic reactions[1,6]. Numerous experimental data confirming this hypothesis have accumulated in recent years. Examples of the one-electron reduction reactions of organic compounds (R−X) are provided by the reactions with alkali metals, organic anions, or other organic electron donors (R′−Y):



$$R-X+Na\rightarrow R-X\overset{\cdot}{-}+Na^{+},$$
$$R-X+RO^{-}\rightarrow R-X\overset{\cdot}{-}+RO^{\cdot},$$
$$RX+R':Y\rightarrow R-X\dot{\div}\quad+\quad R'-Y\dot{+}$$
$$R-X\dot{\div}\rightarrow R^{\cdot}+X^{-}\ \text{or}\ R^{-}+X^{\cdot};\qquad R'-Y\dot{+}\rightarrow R'^{\cdot}+Y^{+}\ \text{or}\ R'^{+}+Y^{\cdot}$$

In certain cases several electrons can apparently be transferred in a single stage in oxidation-reduction reactions[7]. This hypothesis is based on the general postulate that a many-electron process taking place in one stage requires a smaller expenditure of energy than the overall energy required for the consecutive transfer of several electrons.

One-electron reduction (oxidation) reactions of molecules inevitably lead to the formation of radicals (radical-ions), which may be reduced (oxidised) in the presence of the same donors (acceptors). It has been convincingly demonstrated in many instances that the oxidation of organic compounds leads to the formation of radicals

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† The 1st All-Union Symposium on "Oxidation-Reduction Reactions of Free Radicals", organised by the Scientific Councils for Chemical Kinetics and Structure of the USSR Academy of Sciences and the Ukrainian SSR Academy of Science jointly with the Pisarzhevskii Institute of Physical Chemistry of the Ukrainian SSR Academy of Sciences (Chairman of Organising Committee—Corresponding Member of the Ukrainian SSR Academy of Sciences V.D. Pokhodenko) was held in Kiev during October, 1976 [see G.A.Kovtun and I. I. Moiseev, Koord. Khim., 3, 4439 (1977)]).

which are then also oxidised. Thus under certain conditions phenols are oxidised via the reactions‡ [8]

$$\mathrm{PhOH} \xrightarrow{-e} \mathrm{PhO}^{\cdot} + \mathrm{H}^{+} \quad ,$$
$$\mathrm{PhO}^{\cdot} \xrightarrow{-e} \mathrm{PhO}^{+} \quad .$$
$$\mathrm{PhO}^{+} + \mathrm{PhOH} - \text{products} + \mathrm{H}^{+} \cdot$$

The oxidation of BPh_4^- proceeds as follows[9]:

$$\mathrm{BPh}_4^- \xrightarrow{-e} \mathrm{BPh}_4^{\cdot} \xrightarrow{-e} \mathrm{BPh}_4^+ \quad ,$$
$$\mathrm{BPh}_4^+ \rightarrow \mathrm{PhPh} + \mathrm{BPh}_2^+ \xrightarrow{\mathrm{H_2O}} \mathrm{Ph_2BOH} + \mathrm{H}^+ \quad .$$

The problem of the quantitative estimation of the ability of unstable radicals to be oxidised or reduced arises in this connection.

Owing to the development of pulse techniques for the investigation of fast reactions and particularly the wide availability of pulse radiolysis apparatus, it is now possible to measure fairly accurately the rate constants for electron transfer reactions involving radicals. Such reactions are important both for chemical kinetics and the chemistry of free radicals, on the one hand, and for testing the postulates of the electron transfer theory, on the other.

1. The Electron Transfer Theory

During the last three decades, electron transfer reactions (oxidation-reduction reactions) between metal complexes have been investigated vigorously. It has now become usual to divide them into reactions of the inner-sphere and outer-sphere types (see, for example, Refs. 10 and 11). The inner-sphere electron transfer between reactants X and Y can be represented as follows in a general form:

$$\mathrm{X} + \mathrm{L} + \mathrm{Y} \rightleftarrows \mathrm{XL} + \mathrm{Y} \quad ,$$
$$\mathrm{XL} + \mathrm{Y} \rightleftarrows \mathrm{XLY} \quad ,$$
$$\mathrm{XLY} \rightleftarrows {}^{-}\mathrm{XLY}^{+} \quad ,$$
$${}^{-}\mathrm{XLY}^{+} \rightleftarrows \mathrm{X}^{-} + \mathrm{LY}^{+} \quad ,$$
$$\mathrm{X}^{-} + \mathrm{LY}^{+} \rightleftarrows \mathrm{X}^{-} + \mathrm{L} + \mathrm{Y}^{+} \quad ,$$

where L is the third species, constituting a binding ligand (usually an anion).

In inner-sphere electron transfer reactions the transition state is formed in such a way that the L species plays the role of a "bridge" between two metal centres, ensuring a pathway for electron transfer. There is then a possibility of the simultaneous dissociation (or formation) of a bond between the inner orbitals of the metal ion (usually between the d orbitals). An alternative electron transfer mechanism does not require the presence of a binding ligand and the formation (dissociation) of new bonds and is referred to as the outer-sphere mechanism§.

In certain cases (see, for example, Thornton and Laurence[13]) one distinguishes reactions in the inner sphere where the rate-limiting stage is either substitution:

$$\mathrm{M}^{n+}\mathrm{X}_m + \mathrm{L} \xrightarrow{\text{slow}} \mathrm{M}^{n+}\mathrm{X}_{m-1}\mathrm{L} \xrightarrow{\text{fast}} \mathrm{M}^{(n+1)+}\mathrm{X}_{m-1}\mathrm{L}^-$$

or electron transfer:

$$\mathrm{M}^{n+}\mathrm{X}_m + \mathrm{L} \xrightarrow{\text{fast}} \mathrm{M}^{n+}\mathrm{X}_{m-1}\mathrm{L} \xrightarrow{\text{slow}} \mathrm{M}^{(n+1)+}\mathrm{X}_{m-1}\mathrm{L}^- \quad .$$

The ideas developed for electron transfer between metal complexes have been applied to electron transfer reactions between metal complexes and organic compounds and between organic molecules.

Criteria have been put forward for the determination of the electron transfer mechanism[12,14]. It is extremely likely that the reaction is of the outer-sphere type if the observed rate is higher than the rate at which ligands are substituted in the species being reduced (oxidised). There are also indirect methods for the determination of the electron transfer mechanism[14]. The necessity to know the electron transfer mechanism is due to the fact that a change in the structure of the metal ion or ligand leads to different types of influence on the rate of electron transfer depending on the reaction mechanism.

From the theoretical standpoint, the mechanism of outer-sphere electron transfer reactions is simpler and the theory of such reactions is developing successfully[15,16] The Marcus theory[17-21] is widely used nowadays for the analysis of experimental data for electron transfer in the outer sphere. According to this theory, the rate constant for the reaction determining the rate of the outer-sphere electron transfer,

$$A^m + B^n \underset{k_{ba}}{\overset{k_{ab}}{\rightleftarrows}} A^{m-1} + B^{n+1} \quad ,$$

is given by the following equation:

$$k_{ab} = Z_{ab} \exp(-\Delta G^*/RT), \tag{1}$$

where Z_{ab} is the frequency factor (~10^{11} litre mole^{-1} s^{-1}) and ΔG^* the free energy of activation. The following relation holds for ΔG^*:

$$\Delta G^* = W + \frac{1}{4}\lambda + \frac{1}{2}\Delta G^0_{ab} + \frac{1}{4\lambda}(\Delta G^0_{ab})^2, \tag{2}$$

where W is the Coulombic term expressing the difference between the amounts of work which must be expended to join and separate reactants A^m and B^n, λ the free energy of the rearrangement of the polarised solvent associated with the change in the nature of the spatial distribution of charges on electron transfer, and ΔG^0 the standard free energy of reaction. In electron transfer reactions between radicals and organic molecules one of the reactants is in most instances uncharged and W may be regarded as zero. Eqn. (2) then simplifies:

$$\Delta G^* = \frac{1}{4}\lambda(1 + \Delta G^0_{ab}/\lambda)^2.$$

For the oxidation (reduction) of radical-ions by the initial molecules, we have

$$\Delta G^0_{ab} = 0 \quad \text{and} \quad \Delta G^* = \frac{1}{4}\lambda. \tag{3}$$

If the rate of reaction approaches the diffusional rate, the following expression is used for the observed constant k_{ab}:

$$k_{ab} = k_{\text{diff}}\ k_{\text{act}}/(k_{\text{act}} + k_{\text{diff}}), \tag{4}$$

where k_{act} is the reaction rate constant according to Eqn. (1). If it is assumed that the contribution to the parameter λ is due solely to the reorientation of the solvent molecules, one can estimate the reaction radius r_{ab} by means of the equation[17-21]

$$\lambda_0 = \left(\frac{1}{2r_a} + \frac{1}{2r_b} - \frac{1}{r_{ab}}\right)\left(\frac{1}{D_O} - \frac{1}{D_s}\right)(\Delta ze)^2, \tag{5}$$

where Δz is the number of electrons transferred, r_a and r_b are the polarisation radii of the reactants, D_O is the optical dielectric constant of the solvent (the square of the

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‡ Here and henceforth $Ph=C_6H_5$.

§ It has been suggested[12] that the first mechanism be called the "bonded mechanism" and the second the "non-bonded mechanism" in order to avoid confusion in terminology in connection with the inner-sphere and outer-sphere association of species. However, the generally accepted terminology will be used in the present review.

refractive index), and D_S is the static dielectric constant. It is usually assumed that[22]

$$r_a = r_b = \frac{1}{2} r_{ab}.$$

2. Reactions of Radicals with Nitro-compounds and Other Oxidants

Free radicals are known to react with various electron acceptors—quinones, dyes, nitro-compounds, etc. The study of the reactions of radicals with organic nitro-compounds is of undoubted interest for the elucidation of the mechanism of the radiation-initiated processes in chemical and biological systems. It is suggested that compounds with a sufficiently high electron affinity, particularly aromatic and heterocyclic nitro-compounds, are radiation stabilisers even at low concentrations as a result of secondary reactions involving radicals formed in the biological "targets"[23,26]. The reactions of organic radicals with nitrobenzene, nitromentane, etc. have been investigated by pulse radiolysis and ESR combined with pulse irradiation or the $Ti^{4+}-H_2O_2$ flow system[29-32]. It has been shown that such interactions may involve both addition and electron transfer reactions, the relative contributions of which depend on the nature of the organic radical, the nitro-compound, and the pH of the medium. For example, aliphatic hydroxy-radicals are ionised in an alkaline medium and electron transfer predominates; in neutral solutions, addition to the aromatic ring or the nitro-group is observed together with electron transfer[24].

It has been shown by ESR that α-hydroxy- and α-alkoxy-radicals give up an electron to suitable acceptors[28-30,32]. Alkyl radicals, β-hydroxy-radicals, $OH^{\cdot}$, and $NH_2^{\cdot}$ react with electron acceptors mainly via the addition mechanism[29,33-35].

In the general case radicals participate in oxidation reactions and reactions involving addition to the acceptor. The change in the relative contributions of these reactions as a function of the radical structure can be accounted for by the change in the electron-donating capacity of the radical. It is believed that the electron-donating capacity is characterised by the stability of the carbonium ions obtained from the radicals, which increases in the sequence[30]

$$^{+}CH_2OH < CH_3\overset{+}{C}HOH < (CH_3)_2\overset{+}{C}OH \quad .$$

The tendency towards electron transfer then varies in the sequence[24]

$$(CH_3)_2\dot{C}O^- > CH_3\dot{C}HCO^- > \dot{C}H_2O^- > (CH_3)_2\dot{C}OH > CH_3\dot{C}HOH > \dot{C}H_2OH \quad .$$

The reducing capacity of radicals diminishes in the sequence[25,37]

$$CO_2^{\overline{\cdot}} > (CH_3)_2\dot{C}OH > CH_3\dot{C}HOH > \dot{C}H_2OH \quad .$$

Various organic radicals may be oxidised by hydrogen peroxide and other peroxides[53]. For example:

$$\dot{C}O_2H + (CH_3)_3COOR \rightarrow H^+ + CO_2 + (CH_3)_3C\dot{O} + RO^- \quad .$$

$[R = H$ or $C(CH_3)_3]$. It has been suggested that oxygen may oxidise certain organic radicals via one-electron transfer[53]:

$$R^{\cdot} + O_2 \rightarrow R^+ + O_2^{\overline{\cdot}} \quad .$$

The one-electron oxidation of radicals by oxygen competes with the addition reaction—the formation of a peroxy-radical[53]:

$$R^{\cdot} + O_2 \rightarrow RO_2^{\cdot} \quad .$$

The radical-anions of aromatic compounds and certain quinones also react with oxygen via electron transfer[66,87]:

$$R^{\overline{\cdot}} + O_2 \rightarrow R + O_2^{\overline{\cdot}} \quad .$$

It has been established that the ability of radicals to transfer an electron to O_2 and H_2O_2 varies in the sequence[53]

$$^{\cdot}CO_2H > (CH_3)_2\dot{C}OH > \dot{C}H_2OH > \dot{C}H_2C\,(CH_3)_2OH,$$
$$\dot{C}H_2CH\,(CH_3)\,OH \quad .$$

$CO_2^{\overline{\cdot}}$, a strong reductant, is involved in reductive elimination reactions with various alkyl halides RX:[54]

$$CO_2^{\overline{\cdot}} + RX \rightarrow CO_2 + R^{\cdot} + X^- \quad .$$

One-electron reactions in which $CO_3^{\overline{\cdot}}$ is oxidised by duroquinone, benzoquinone, and 2-methylnaphthoquinone have been discovered[162,167]:

$$\begin{tikzcd}[column sep=small] CO_3^{\overline{\cdot}} + Q \arrow[r] & CO_3 \arrow[dl] \arrow[dr] & + Q^{\overline{\cdot}} \\ CO_2 & + & 1/2O_2 \quad . \end{tikzcd}$$

The kinetics of electron transfer reactions between radicals and electron acceptors have been investigated mainly by pulse radiolysis. The course of the reaction can then be followed from the accumulation of the acceptor radicals, which usually absorb light in a spectral region convenient for recording. A study has been made[23] of the oxidation of the radicals obtained from alcohols by aromatic nitro-compounds. The rate constants for the radical oxidation adduct formation reactions increase with increase of the oxidation-reduction potential of the acceptor. This behaviour appears to be fairly general (see end of Section III). However, when the differences between the oxidation-reduction potentials of the acceptors E^0 are fairly small (for example, amounting to several hundredths or tenths of a volt) and the reaction kinetics approach diffusion kinetics, there may be no correlation (see also the end of Section IV, subsection 1). A relation between the rate constants for electron transfer from $O_2^{\overline{\cdot}}$, $\dot{C}H_2OH$, and $\dot{C}H_2O$ to quinones with a similar structure, on the one hand, and E^0 for the acceptor, on the other, has not been observed in a number of studies[38-40,47].

Many radicals which are important from the biological point of view react with vitamin K_3.[41] The reactions have been investigated by pulse radiolysis. Under the experimental conditions (low doses and low radical concentrations) the rate constants for the reactions of the majority of radicals with vitamin K_3 are $k \geqslant 2 \times 10^8$ litre mole^{-1} s^{-1}¶. More than 90% of the initial radical concentration is then consumed by reaction with the vitamin. Certain radicals are hardly involved in the electron transfer reaction ($k \ll 1 \times 10^8$ litre mole^{-1} s^{-1}) and participate either in the addition to the vitamin or react with one another. The cause of this may also consist in the formation of several types of radicals with different values of E^{01} under the influence of the electron pulse[41].

It has been established that certain oxidation-reduction reactions of aromatic radicals are reversible[22,66,72,157,166]. The semiquinone radical-anions $Q^{\overline{\cdot}}$ are reversibly oxidised by nitroimidazoles S and quinones[72,157]:

$$Q^{\overline{\cdot}} + S \rightleftarrows Q + S^{\overline{\cdot}} \quad ,$$

$$Q_i^{\overline{\cdot}} + Q_j \rightleftarrows Q_i + Q_j^{\overline{\cdot}} \quad .$$

Different radicals of pyridine derivatives, including the product of the one-electron reduction of nicotinamide-adenine dinucleotide ($NAD^{\cdot}$) participate in reversible

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¶ The constants obtained at room temperature are quoted in this review.

reactions involving electron transfer from flavin-adenine dinucleotide (FAD):[160]

$$\mathrm{NAD^{\cdot} + FAD \rightleftharpoons NAD^{+} + FAD^{\cdot -}}$$

The kinetics of numerous electron transfer reactions with participation of free radicals, investigated mainly by pulse radiolysis, have been analysed[22]. It has been established that the experimental data obey the Marcus theory; a satisfastory correlation has been found between $\lg k_{ab}$ and ΔG^{0}_{ab} with $\lambda \simeq 18$ kcal mole^{-1}.[22] Three groups of reactions with participation of radical-anions were examined:

$$\mathrm{O_2^{\cdot -} + Q \rightleftarrows O_2 + Q^{\cdot -}}$$

$$\mathrm{RNO_2^{\cdot -} + DQ \rightleftarrows DQ^{\cdot -} + RNO_2}$$

$$\mathrm{Q^{\cdot -} + Q^{\cdot -} \rightleftarrows Q + Q^{2-}} \text{ (disproportionation of semiquinones),}$$

where Q are 1,4-quinones, $\mathrm{RNO_2^{\cdot -}}$ are aromatic radical-anions, and DQ is duroquinone.

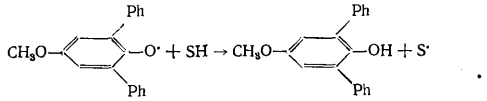
Using Eqn.(5), $r_{ab} \simeq 10$ Å, which is the distance between the centres of the reactants in the transition state for which electron transfer takes place in the given reactions, was obtained.

3. Radical Reduction Reactions

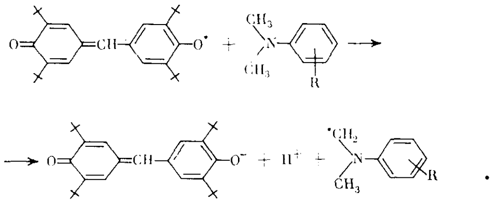
The simplest example of radical reduction reactions is the abstraction of a hydrogen atom from a suitable substrate:

$$\mathrm{R_1^{\cdot} + R_2H \rightarrow R_1H + R_2^{\cdot}} \quad . \qquad (6)$$

Reactions of type (6) have been investigated in detail in studies on liquid-phase chain oxidation reactions of hydrocarbons[2]. Reaction (6) with $\mathrm{R_1^{\cdot} = OH^{\cdot}}$ constitutes a common method for the generation of various free radicals (see Section VI, Subsection 1)†. Phenoxy-radicals are capable of being reduced to phenols by oxidising solvents containing mobile hydrogen atoms, for example[42]:



It has been shown[43-46] that stable phenoxy-radicals oxidise organic compounds without mobile H atoms via electron transfer:



(7)

Galvinoxy- and indophenoxy-radicals are reduced to the corresponding phenoxide ions by reaction with $\mathrm{OH^-}$ and

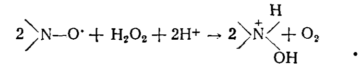
.[85,103]

The inorganic radical species $\mathrm{SO_4^{\cdot -}}$, $\mathrm{CO_3^{\cdot -}}$, $\mathrm{\dot{C}O_3H}$, and $\mathrm{Br_2^{\cdot -}}$ oxidise disulphides[137], and $\mathrm{Br_2^{\cdot -}}$, $\mathrm{CO_3^{\cdot -}}$, and $\mathrm{(SCN)_2^{\cdot -}}$ oxidise tryptophan[163]. These reactions proceed via one-electron transfer. The quenching of the triplet state of pyrene in micelles by the radical-anion $\mathrm{Br_2^{\cdot -}}$ involves the same mechanism[171]:

$$\mathrm{{}^{3}P_{\mathit{mic}} + Br_2^{\cdot -} \rightarrow P^{+}_{\mathit{mic}} + 2Br^{-}} \quad .$$

The radical obtained when e^{-}_{aq} interacts with $\mathrm{SF_6}$ (tentatively identified as $\mathrm{SF_5^{\cdot}}$) is an extremely powerful oxidant, more active than $\mathrm{SO_4^{\cdot -}}$ and $\mathrm{Cl^{\cdot}}$ [159]. It can be used for the effective generation of other free radicals.

In an acid medium nitroxy-radicals are powerful oxidants. The 2,2,6,6-tetramethylpiperidinyloxy-radical oxidises $\mathrm{H_2O_2}$.[84] The overall reaction equation is

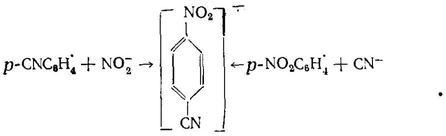


$$2\,{>}\mathrm{N{-}O^{\cdot} + H_2O_2 + 2H^{+} \rightarrow 2\,{>}\overset{+}{N}(H)(OH) + O_2} \quad .$$

In the presence of various anions, active free radicals participate in competing reactions[48]:

$$\mathrm{R^{\cdot} + A^{-}} \begin{cases} \xrightarrow{a} \mathrm{[R-A]^{\cdot -}} & (8a) \\ \xrightarrow{b} \mathrm{R^{-} + A^{\cdot}} \quad . & (8b) \end{cases}$$

The relative contributions of reactions (8a) and (8b) depend on many factors—the stability of the radical-anion $\mathrm{[R{-}A]^{\cdot -}}$ and the ease of the oxidation of $\mathrm{A^-}$ and the reduction of $\mathrm{R^{\cdot}}$. The unsubstituted phenyl radical adds to $\mathrm{NO_2^-}$ or to $\mathrm{(CH_3)_2C{=}NO_2^-}$, forming the $\mathrm{[R{-}A]^{\cdot -}}$ species, which have been detected by ESR. *p*-Nitrophenol or *p*-cyanophenyl radicals possess powerful electron-accepting properties and, in the presence of a readily oxidisable species $\mathrm{A^-}$, reaction (8b) takes place. The $\mathrm{NO_2^-}$ and $\mathrm{CN^-}$ species, which are more resistant to oxidation, react with these radicals via reaction (8a):



Many organic synthetic reactions involve the competing processes (8a) and (8b) as the intermediate stage[48].

The equilibrium

$$\mathrm{[R-A]^{\cdot -} \rightleftarrows R^{-} + A} \qquad (9)$$

may be postulated. Electron transfer then takes place with the preliminary formation of $\mathrm{[R{-}A]^{\cdot -}}$, i.e. via reactions (8a) and (9).

4. Oxidation (Reduction) of Radical-anions by the Initial Compounds

The kinetics of electron exchange reactions between organic molecules and the corresponding radical-anions and radical-cations are usually investigated by ESR; the radicals are then generated by various methods, for example by electrochemical reduction (oxidation)[49-51].

The reactions of phenothiazine, 10-methylphenothiazine, phenoxazine, and phenoxanthine radical-cations have been investigated[51]. Much attention has been devoted to the radical-anions derived from compounds such as benzonitrile, phthalonitrile, terephthalonitrile, pyromellitonitrile, 4-cyanopyridine, and a number of others. The ability of the initial neutral molecules to accept an electron is characterised by the rate constant for the reaction

$$\mathrm{R^{\cdot -} + R \xrightarrow{k_{10}} R + R^{\cdot -}} \qquad (10)$$

and the ability to give up an electron is characterised by the constant k_{11}:

$$\mathrm{R^{\cdot +} + R \xrightarrow{k_{11}} R + R^{\cdot +}} \quad . \qquad (11)$$

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† In many instances (for example, when $\mathrm{R_2H}$ is an aromatic compound) the formation of $\mathrm{H_2O}$ and $\mathrm{R_2^{\cdot}}$ is preceded by the formation of the adduct $\mathrm{HOR_2H}$.

The above assumption is equivalent to the hypothesis that there is a correlation between the values of $\lg k_{10(11)}$ and certain quantities which may be either calculated or measured. The ability of the molecule to accept an electron is associated with its electron affinity, which in the simplest molecular orbital method is believed to be equal to $-E$, E being the energy of the lowest vacant orbital of the initial molecule. The quantity $\lg k_{10}$ should also be correlated with the electrochemical reduction half-wave potentials $E_{1/2}$. Analogous correlations are to be expected between the values of $\lg k_{11}$, the energies of the highest occupied molecular orbitals (HOMO) of R, and the corresponding oxidation potentials.

Entirely satisfactory correlations have been found between $\lg k_{11}$ and E_{HOMO} and between $\lg k_{11}$ and $E_{1/2}$.[51] Such correlations show that the energy required to remove an electron from the initial molecule may have a decisive influence on k_{11}. An analogous correlation has been obtained for reaction (10) between $\lg k_{10}$ and $E_{1/2}$. Solvation apparently plays an important role for radical-anions and it is not surprising that the values of $\lg k_{10}$ are better correlated with experimental high-wave potentials $E_{1/2}$.[51]

In the electron exchange between a quinone and the corresponding semiquinone, i.e.

$$Q^{\overline{\cdot}} + Q \rightleftarrows Q + Q^{\overline{\cdot}}$$

no correlation was observed between the rate of electron exchange and the reduction potential of the quinone[157], with no change in geometry in the course of the reaction; the authors[157] believe that the correlations observed[51] between $\lg k_{10}$ and $E_{1/2}$ reflect certain geometrical changes following electron transfer from radical-anions to the initial molecule.

The change in the geometry of the species during the reaction can have a significant influence on the rate constant for electron transfer. For example, the rate constant for the reaction involving cyclo-octatetraene

$$R^{\overline{\cdot}} + R^{2-} \rightarrow R^{2-} + R^{\overline{\cdot}} \tag{12}$$

is $k_{12} \simeq 10^9$ litre mole^{-1} s^{-1}, while $k_{10} \simeq 10^5$ litre mole^{-1} s^{-1} or less[52]. The difference is probably caused by the fact that the $R^{\overline{\cdot}}$ and R^{2-} species derived from the given molecule are planar while R is non-planar[52].

It is possible to estimate theoretically the rate constant for the electron exchange between the initial molecule and the radical-ion in water. Using Eqns.(1) and (3) and the value $\lambda \simeq 18$ kcal mole^{-1},[22] one obtains $k_{10(11)} \simeq 5 \times 10^7$ litre mole^{-1} s^{-1}. Indeed, $k_{10} = 1 \times 10^7$ litre mole^{-1} s^{-1} has been found for the radical-anion $(CH_3)_2CO^{\overline{\cdot}}$.[22] $k = 1 \times 10^8$ litre mole^{-1} s^{-1} for the exchange between the phenoxy-radical and the phenoxide ion[22]. The exchange reaction between the nitromethane radical-anion and nitromethane has a rate constant $k_{10} < 3 \times 10^5$ litre mole^{-1} s^{-1}.[22] Such a low value of k_{10} is probably due to the significant geometrical changes accompanying the radical-anion–molecule transition. The upper limit to the values of k_{11} for the reaction

$$H^+ + H \rightleftarrows H + H^+$$

is 5×10^5 litre mole^{-1} s^{-1}. The low value of k_{11} is associated with the extremely high solvation energy of H^+.[22]

5. The Influence of the Solvent on Electron Transfer Reactions

Reactions (10) and (11) take place between species which are dipoles and between an ion and a dipole. In a solution with a macroscopic dielectric constant D the interaction energy between an ion and a dipole is expressed as follows:

$$E_{13} = ze\mu \cdot \cos(\theta/Dr^2), \tag{13}$$

where μ is the permanent dipole moment and ze the ionic charge; the orientations of the ion and the dipole are illustrated in Fig.1; $E_{13} = E_{\max}$ when $\theta = 0$. The interaction energy between two dipoles reaches a maximum when they are arranged "head-to-tail" along a straight line:

$$E_{14} = -\frac{2\mu_1\mu_2}{Dr^3} \quad . \tag{14}$$

The maximum interaction energy between a dipole-anion and a dipole is then given by the expression

$$E_{15} = -\mu_1\left(e + \frac{2\mu_2}{r}\right)\Big/Dr^2 \quad . \tag{15}$$

For example, $E_{15} = 1.0$ kcal mole^{-1} is obtained for $\mu_1 = \mu_2 = 4D$, $r = 4$ Å, and $D = 35$, and we have $E_{13} = \frac{2}{3}E_{15}$.[51]

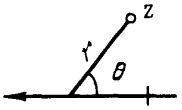

Figure 1. The mutual orientation of the ion and the dipole.

One may assume that the rate constant for electron transfer is given by the equation

$$k = Ae^{-(E_a + E_{15}/RT)} , \tag{16}$$

where A is independent of the solvent and E_a incorporates all other factors contributing to the activation energy which are independent of the solvent[51]. One can then write $k = Z'e^{-E_{15}/RT}$ $(Z' = Ae^{-Ea})$ or

$$\ln k = \ln Z' + \mu_1(e + 2\mu_2/r)/RTDr^2. \tag{17}$$

Eqn.(17) predicts a decrease of the rate constant with increase of the dielectric constant of the solvent. Such a tendency has been observed for reactions (10) and (11) in many solvents, with the exception of dioxan[51]. However, one must bear in mind that dioxan has a very low dielectric constant ($D = 2$); the formation of bound ion pairs in such a solvent may play a significant role and may affect the constant.

If the values of $\mu(R)$ and $\mu(R^{\overline{\cdot}})$ are known‡, it is possible to obtain from the experimental relations (17) the distance r between the reactants for which electron transfer takes place. Thus $r \simeq 4$ Å has been obtained for the benzonitrile radical-anion[51].

A study of the unimolecular reaction

$$^{\overline{\cdot}}NfCH_2 - C_6H_{10} - CH_2Nf \rightleftarrows NfCH_2 - C_6H_{10} - CH_2Nf^{\overline{\cdot}}$$

(Nf = α-naphthyl; the $NfCH_2$ substituents are in the 1,4-positions in cyclohexane) established that electron transfer requires the mutual approach of the naphthalene rings to a distance not greater than 7–9 Å.[50] The authors believe

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‡ It is sometimes assumed that $\mu(R^{\overline{\cdot}}) = \mu(R)$.[51]

that electron transfer does not require a close approach of the reactants, in contrast to the reactions involving the formation of excimers, exciplexes, and charge-transfer complexes.

The electron exchange reaction between benzoquinone (duroquinone) and the corresponding semiquinone (durosemiquinone) involves a radius of 5–6 Å; the molecular radii of the species are smaller approximately by 1.5 Å. Presumably a monomolecular solvation shell remains around the reacting species at the instant of electron transfer[157].

The Marcus theory may be tested by studying the influence of the solvent on $k_{10(11)}$. Since in many instances the values of $k_{10(11)}$ are comparable to those of k_{diff}, it is useful to employ Eqn.(4). It follows from Eqns.(3) and (5) that $\lg k_{10(11)}$ should increase with decrease of the parameter $D_{\text{o}}^{-1} - D_{\text{s}}^{-1}$. However, the experimental values of $\lg k_{\text{obs}}$ and $\lg k_{\text{ab}}$ decrease as the above parameter diminishes[51]. In the Marcus theory Z is independent of the solvent. Nevertheless, there is a satisfactory linear correlation between $\lg k_{\text{obs}} - \lg k_{\text{diff}}$ and $D_{\text{o}}^{-1} - D_{\text{s}}^{-1}$; the corresponding plot has a negative slope[51]. Thus in many cases agreement between experiment and the Marcus theory requires the introduction of additional parameters, in particular, one must assume that the frequency factor depends on the solvent.

The influence of the solvent on the kinetics of reaction (10) has been investigated[49] using the radical-anion derived from *N*-(n-butyl)phthalimide as $\text{R}^{\overline{\cdot}}$. It was observed that k_{10} depends little on the solvent (hexamethylphosphoramide, 1,2-dimethoxyethane, dimethylformamide, acetonitrile, and propionitrile) despite the marked differences between the solvent viscosities and it was found that $k_{10} \simeq 3 \times 10^8$ litre mole^{-1} s^{-1}, which is less than k_{diff} for all the solvents and is close to its value for hexamethylphosphoramide. The activation energies E_{10} are higher by approximately 1 kcal mole^{-1} than the corresponding activation energies for the viscous flow of the solvents. The comparatively high values of E_{10} imply that the ions are surrounded by weakly oriented solvent molecules, which undergo a rearrangement in the transition state. The reaction is slower in 1,2-dimethoxyethane than in the other solvents; E_{10} is greater than the activation energy for the viscous flow of this solvent by 1.6 kcal mole^{-1}, which can be accounted for by the formation of ion pairs in this ether[49]. The above effect can be observed in other solvents when the concentration of the supporting electrolyte is increased[49].

The polarity of the medium has a significant influence on the kinetics of the one-electron reduction of the galvinoxy- and indophenoxy-radicals by substituted amines [reaction (7)].[43] The rate of reaction increases with increase of the polarity of the medium, so that the dipole moment of the activated complex in the transition state is greater than the sum of the dipole moments of the reactants. The experimental values of k_7 are described satisfactorily by the relation[43]

$$\lg k_7 = \lg k_0 - \frac{A}{T} \cdot \frac{D-1}{2D+1},$$

where A is the constant.

The influence of solvent (water–alcohol) composition on the kinetics of the following reactions has been investigated by pulse radiolysis[55]:

$$\text{CH}_3\text{CHO}^{\overline{\cdot}} + \text{C}_6\text{H}_5\text{NO}_2 \rightarrow \text{CH}_3\text{CHO} + \text{C}_6\text{H}_5\text{NO}_2^{\overline{\cdot}} \quad ,$$

$$\text{CH}_3\text{C}_6\text{H}_5\text{CO}^{\overline{\cdot}} + \text{C}_6\text{H}_5\text{NO}_2 \rightarrow \text{CH}_3\text{C}_6\text{H}_5\text{CO} + \text{C}_6\text{H}_5\text{NO}_2^{\overline{\cdot}} \quad ,$$

$$\text{CH}_3\text{CHO}^{\overline{\cdot}} + (\text{C}_6\text{H}_5)_2\text{CO} \rightarrow \text{CH}_3\text{CHO} + (\text{C}_6\text{H}_5)_2\text{CO}^{\overline{\cdot}} \quad ,$$

$$\text{CH}_3\text{C}_6\text{H}_5\text{CO}^{\overline{\cdot}} + (\text{C}_6\text{H}_5)_2\text{CO} \rightarrow \text{CH}_3\text{C}_6\text{H}_5\text{CO} + (\text{C}_6\text{H}_5)_2\text{CO}^{\overline{\cdot}} \quad .$$

The rate constants for these reactions in water vary from 8×10^8 to 3×10^9 litre mole^{-1} s^{-1}, which is close to the value of k_{diff}.[56] The solvent was found to have a stronger influence on slow reactions than on fast reactions. There is no regularity in the influence of the solvent on the rate of reactions with the same functional groups and the kinetic parameters of reactions vary in a complex manner with the composition of the binary mixtures[55]. The observed relations cannot be accounted for with the aid of the Marcus theory. In this and other electron transfer theories the activation energy required for the reaction refers solely to the ion–solvent interaction, the solvent being regarded as a continuum[15,17,19]. It appears that a deeper understanding of the influence of the solvent on the rate of electron transfer requires allowance for the microscopic properties of the solvent surrounding the reaction species[55].

III. OXIDATION–REDUCTION POTENTIALS OF FREE RADICALS

The knowledge of the one-electron oxidation-reduction potentials of radicals (E^{01} at pH 7.0 and approximately 25°C) could serve as a basis for the prediction of the directions and rates of the oxidation-reduction reactions of these species. Waters and Mackinnon[58] noted the important role of the oxidation-reduction potentials in the elucidation of the directions of radical reactions. They suggested that free radicals and the corresponding cations or anions form pairs of reversible oxidation-reduction systems, i.e.

$$\text{R}^{\cdot} \rightleftarrows \text{R}^{+} + \text{e}; \quad \text{R}^{\cdot} + \text{e} \rightleftarrows (\text{R:})^{-}$$

to which correspond two different oxidation-reduction potentials $E_{(-\text{e})}$ and $E_{(+\text{e})}$. A simple procedure was proposed for the estimation of $E_{(-\text{e})}$. The radicals which are involved in the chain oxidation of the initial compound RH by Fenton's reagent take part in the reaction[58]

$$\text{R}^{\cdot} + \text{Fe}^{3+} \rightarrow \text{R}^{+} + \text{Fe}^{2+}; \quad \text{R}^{+} + \text{H}_2\text{O} \rightarrow \text{ROH} + \text{H}^{+} .$$

Consequently $E_{(-\text{e})} < 0.74$ V for these radicals. (The potential of the $\text{Fe}^{2+}|\text{Fe}^{3+}$ pair is +0.74 V at pH 0.[58])

The ability of the radical to be oxidised has been studied in connection with investigations of the mechanism of the Kolbe electrosynthesis[59,60]. During this process, the oxidation of the carboxylate ion at the anode

$$\text{RCOO}^{-} \rightarrow \text{R}^{\cdot} + \text{CO}_2 + \text{e}^{-}$$

is followed by further oxidation of $\text{R}^{\overline{\cdot}}$ to the carbonium ion:

$$\text{R}^{\cdot} \rightarrow \text{R}^{+} + \text{e}^{-}, \tag{18}$$

provided that the ionisation potential I of the radical is less than 8 eV.[59] A linear relation has been observed between I (determined by the electron impact method) and the potential of the electrode at which reaction (18) takes place[59]. (One should also note that there is a linear correlation between the values of I for radicals, determined by the electron impact method, and the energies of the highest occupied molecular orbitals[59].)

In many cases the values of E^{01} can be calculated from known thermodynamic quantities. $E^{01}(\text{CO}_2|\text{CO}_2^{\overline{\cdot}}) = -1.8$ V [170] and $E^{01}(\text{O}_2|\text{O}_2^{\overline{\cdot}}) = -0.16$ V [150] were evaluated in in this way.

The experimental determination of the values of E^{01} for short-lived free radicals involves certain difficulties associated with the necessity to generate radicals and to measure the values of E^{01} rapidly before the radicals are destroyed.

The potentials E^{01} for the reactions of short-lived radicals with electron acceptors and donors have been determined[39,61-64], using mainly dyes and quinonoid compounds as acceptors. The study of the interaction of dyes with radicals is of special interest, since various photochemical and radiation-chemical one-electron reduction reactions of dyes yield substrate radicals capable of reacting with the dye molecules. The proposed method is based on the investigation of the ability of the free radicals $^{\cdot}RH$ to participate in electron transfer reactions with various acceptors A, whose oxidation-reduction potentials are known:

$$^{\cdot}RH + A \rightleftarrows R + A^{\cdot-} + H^+ \quad . \tag{19}$$

Depending on the pH of the aqueous solution, the radical species $^{\cdot}RH$ or $A^{\cdot-}$ were found to exist either in the acid or basic form:

$$^{\cdot}RH \rightleftarrows R^{\cdot-} + H^+ \quad ,$$
$$^{\cdot}AH \rightleftarrows A^{\cdot-} + H^+ \quad .$$

The studies were performed by pulse radiolysis and kinetic spectrophotometry. The course of reaction (19) was monitored by following the formation of $A^{\cdot-}$ (or the protonated form $^{\cdot}AH$) or the "decolorisation" of the acceptor (usually a dye in such cases).

It was observed that the plot of the efficiency of electron transfer, expressed as a percentage, against E^0 for the acceptors (donors) is a curve analogous to a titration curve (Fig. 2*a*). The value of E^0 corresponding to 50% electron transfer was used to calculate E^{01} for the radical[39,52-64]. Thus one-electron potentials were obtained by means of a comparison with the known two-electron potentials, which is not entirely correct. If a correlation is observed between the two-electron potentials and any parameter associated with the one-electron transfer (such as the rate of electron transfer or the energy of the lowest vacant orbital), this implies in essence that in the given instance there is a correlation between the one- and two-electron potentials[164].

Furthermore, in the calculation of E^{01} it was implicitly assumed that equilibrium (19) can be attained and the Nernst equation was used. However, additional experiments showed that there is insufficient time for the attainment of equilibrium (19) during the experimental time interval. For example, the oxidation of the lactic acid radical,

$$CH_3\dot{C}(OH)COO^- + A \rightarrow CH_3COCOO^- + A^{\cdot-} + H^+$$

leads to the formation of pyruvate ions, but the observed rate of formation of the radicals $A^{\cdot-}$ is independent of $[CH_3COCOO^-]$. Thus there is insufficient time for the attainment of equilibrium and the reverse reaction is very slow ($k_{-10} \leqslant 10^6$ litre mole^{-1} s^{-1}) compared with the observed value $k_{19} = 3.0 \times 10^9$ litre mole^{-1} s^{-1}.[64] An analogous situation was observed also for the other radicals investigated, so that Eqn. (19) is inapplicable. One must therefore consider only the reaction

$$^{\cdot}RH + A \rightarrow R + A^{\cdot-} + H^+ \quad . \tag{20}$$

"Titration" curves (Fig. 2*a*) are obtained as a result of competition between radicals (20) and (21) (mechanism I):

$$^{\cdot}RH + {}^{\cdot}RH \rightarrow \text{products} \quad . \tag{21}$$

and (or) between reactions (20) and (22) (mechanism II)

$$^{\cdot}RH + A \rightarrow {}^{\cdot}RHA \ (\text{addition of radical}) \quad . \tag{22}$$

For the majority of radicals investigated, mechanism I does not apparently play a significant role, since it has been found that under the experimental conditions the efficiency of the formation of $A^{\cdot-}$ (expressed as a percentage) is independent of the ratio $[A]/[^{\cdot}RH]$ in the range of the latter 15–100.

We shall now consider in greater detail mechanism II involving competition between oxidation [reaction (20)] and addition [reaction (22)] reactions. The following expressions can be formulated[23,64]:

$$-\frac{d[^{\cdot}RH]}{dt} = \frac{d[A^{\cdot-}]}{dt} + \frac{d[^{\cdot}RHA]}{dt} = (k_{20} + k_{22})[^{\cdot}RH]\cdot[A] \quad . \tag{23}$$

Taking into account the relation

$$\frac{d[A^{\cdot-}]}{dt} = k_{20}[^{\cdot}RH]\ [A], \tag{24}$$

we obtain

$$-\frac{d[^{\cdot}RH]}{dt} = \frac{k_{20} + k_{22}}{k_{20}}\frac{d[A^{\cdot-}]}{dt}. \tag{25}$$

Integration with respect to time from zero to t gives

$$[^{\cdot}RH] = [^{\cdot}RH]_0 - \frac{k_{20} + k_{22}}{k_{20}}[A^{\cdot-}] \tag{26}$$

or substituting the resulting expression for $[^{\cdot}RH]$ in Eqn. (24), we obtain the relation

$$\frac{d[A^{\cdot-}]}{dt} = k_{20}[^{\cdot}RH]_0[A] - (k_{20} + k_{22})[A][A^{\cdot-}]. \tag{27}$$

Provided that reaction (20) has reached completion $\{d[A^-]/dt = 0\}$, it is possible to obtain from Eqn. (27)

$$\frac{[A^{\cdot-}]}{[^{\cdot}RH]_0} = \frac{k_{20}}{k_{20} + k_{22}} = \frac{[R]}{[^{\cdot}RH]_0}. \tag{28}$$

The quantity $[R]/[^{\cdot}RH]_0$ is called the "percentage electron transfer". Consequently, we finally obtain the following expression for the reaction rate constant[23]:

$$k_{20} = k_{\text{obs}} \cdot (\text{percent electron transfer}), \tag{29}$$

where $k_{\text{obs}} = k_{20} + k_{22}$. Fig. 2 presents relations between k_{20} and the oxidation-reduction potentials E^0 of the acceptors used for the one-electron oxidation of the lactic acid radical and the dependence of the percentage electron transfer on E^0 at the same instant after the electron pulse. The constants k_{obs} and the percentage electron transfer were also independent of the ratio $[A]/[RH^{\cdot}]$ in the range 15–100. Examination of Fig. 2 and Eqn. (29) permits the following conclusions:

1. The reaction of the radical with acceptors involving 100% electron transfer (the upper plateau in Fig. 2*a*) is very close to a diffusion-controlled process. In this case $k_{20} = k_{\text{obs}}$ and $k_{22} \ll k_{20}$, i.e. reaction (22) is unimportant.
2. For reactions with 0% electron transfer (the lower plateau in Fig. 2*a*), we have $k_{20} \ll 10^7$ litre mole^{-1} s^{-1}.

In the intermediate region the efficiency of electron transfer depends on the ratio k_{20}/k_{22}. It is believed[64] that k_{20} depends strongly on E^0 for the acceptor, while k_{22} varies comparatively little over a narrow range of ΔE^0 values (here one must apparently assume that the chemical nature of the acceptor also changes little). Consequently, the observed changes in the "titration" curve reflect mainly the changes in k_{20} and in the observed efficiency of the electron transfer reaction (20) as a function of E^0 for the acceptor.

Thus the method proposed[62,63] does not yield the true oxidation-reduction potentials of free radicals. The potentials corresponding to 50% electron transfer on the "titration" curves must be regarded as "kinetic" potentials E_k^{01} based on two-electron oxidation-reduction potentials of the acceptor (donor)[64]. The values of E_k^{01} are fairly close to those of E^{01}.[61-64] The differences between the numerical values are due to the fact that corrections based on the Nern equation are not used in the determination of E_k^{01}. $E^{01} < E_k^{01}$ for the oxidation of free radicals and $E^{01} > E_k^{01}$ for their reduction. The E_k^{01} scale is of definite practical value for the prediction of the rates of radical reactions. It has been found for a large class of radicals that the values of E_k^0 explain correctly the course of one-electron reactions between these radicals and the electron donors and acceptors[39,62,64,65].

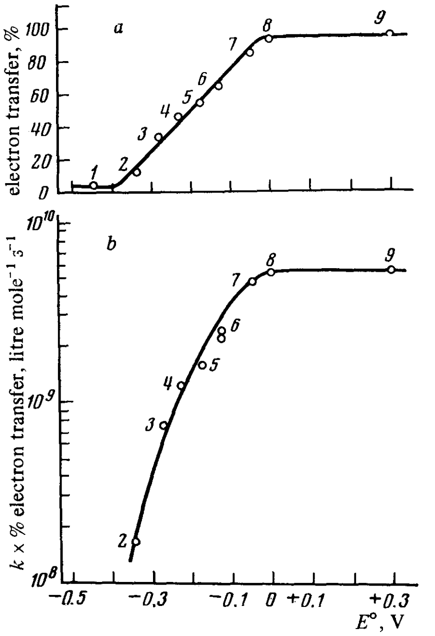


Figure 2. The one-electron oxidation of the $CH_3\dot{C}(OH)CO_2^-$ radical by different acceptors A in aqueous solution[64]: *a*) dependence of the percentage electron transfer on E^0 of the acceptor; *b*) variation of the observed rate constant for the destruction of the radical multiplied by the percentage electron transfer. The same acceptors are designated by identical numerals; the data were obtained after the elapse of the same time interval from the pulse.

The oxidation-reduction potentials of radicals make it possible to account for the relation between the ratio of the rate constants for the oxidation and addition reactions, on the one hand, and the radical structure, on the other (see Section II). Measurements of E^{01} and E_k^{01} [39,62-64] have shown that the basic forms of all the radicals investigated are stronger reductants than the acid forms. For example, $E_k^{01}[CH_3\dot{C}(OH)COOH] > E_k^{01}[CH_3\dot{C}(OH)COO^-] > E_k^{01}[CH_3\dot{C}(O^-)COO^-]$, the corresponding values being +0.16, −0.20, and −0.34 V respectively.

Electron transfer reactions may require considerable activation energies. Despite the favourable relation between the thermodynamic potentials E^{01} of the radical (provided that it is known accurately) and the acceptor (donor), the reaction cannot proceed in this case at a rate sufficient to be able to compete with other radical destruction pathways, for example, reaction (21). The kinetic potentials characterise the ability of the radical to reduce the acceptor (or to oxidise the donor) in kinetic competition with other reactions[64].

For simple aliphatic radicals and the radicals of pyrimidine basis which have been investigated[62-64], reaction (20) is not reversible[64], but the radical-anions derived from quinones and aromatic and heterocyclic nitro-compounds as well as $O_2^{\overline{\cdot}}$ participate in reversible reactions with quinones Q (see the end of Section II, subsection 2):

$$X^{\overline{\cdot}} + Q \rightleftarrows X + Q^{\overline{\cdot}} \quad . \tag{30}$$

The true one-electron potentials at pH 7.0 have been determined for these radical-anions by pulse radiolysis[36,164-166]. These quantities have been designated by E_7^1.

Equilibrium (30) is established fairly rapidly; the destruction of radicals via the $X^{\overline{\cdot}} + X^{\overline{\cdot}}$ and $Q^{\overline{\cdot}} + Q^{\overline{\cdot}}$ reactions is much slower[36,164-166]. It has been shown that the observed spectral changes are caused solely by electron transfer. The observed first-order reaction rate constant (relaxation to the equilibrium value) is given by the relation

$$k_{obs} = k_{30}[Q] + k_{-30}[X].$$

In order to measure the one-electron potential $E_7^1(X|X^{\overline{\cdot}})$, the values of $K_{30} = \{[Q^{\overline{\cdot}}][X]/[X^{\overline{\cdot}}][Q]\}$ were obtained, Q being the reference quinone whose one-electron potential is known§. In order to calculate K_{30}, the concentrations of all the reactants under equilibrium conditions were determined, whereupon $E_7^1(X|X^{\overline{\cdot}}) = E_7^1(Q|Q^{\overline{\cdot}}) - 0.059 \lg K_{30}$.[164]

$E_7^1(O_2|O_2^{\overline{\cdot}}) = -0.155$ V was obtained by this method[164], in agreement with the calculated value[150] (see above). The values $E_7^2(O_2^{\overline{\cdot}}|O_2^{2-}) = 0.865$ V, $E_7^2(DQ^{\overline{\cdot}}|DQ^{2-}) = 0.355$ V, $E_7^1(MQ|MQ^{\overline{\cdot}}) = -0.203$ V, and $E_7^1(BQ|BQ^{\overline{\cdot}}) = 0.1$ V were also obtained (MQ = 2-methyl-1,4-naphthoquinone and BQ = 1,4-benzoquinone) together with the one-electron potentials of many other quinones and nitro-compounds[36,164-166].

It is believed that mainly the nitro-group is involved in electron transfer from the nitro-compound RNO_2 and from the radical-anions of nitro-compounds[165]. It is therefore reasonable to seek a relation between the spin density at the nitro-group and the one-electron potentials of the radicals. The correlation $E^{01}(RNO_2|RNO_2^{\overline{\cdot}}) = 0.315 - 0.054a_{NO_2}^{N}$ (volts) has been found[165]. Thus the lower the spin density at the nitro-group, the smaller the absolute value of the negative one-electron potential. Consequently, the one-electron oxidation-reduction potentials of the radical-anions of nitro-compounds can be obtained from ESR spectra, provided that certain precautions are observed[36].

The radical-anions $RNO_2^{\overline{\cdot}}$, for which $E_7^1(RNO_2|RNO_2^{\overline{\cdot}}) < E_7^1(DQ|DQ^{\overline{\cdot}})$, react effectively with DQ, whereupon the constants k_{30} vary in the range $3 \times 10^8 - 1 \times 10^8$ litre mole^{-1} s^{-1}.[36] On average, k_{30} increases as E_7^1 decreases[36].

---

§ The value $E_7^1(DQ|DQ^{\overline{\cdot}}) = -0.235$ V was obtained for the first time for duroquinone (DQ) in a study by Meisel and Czapski[164].

Strictly speaking, one should not expect a clear-cut correlation between the rate of electron transfer and the difference between the one-electron potentials $\Delta E\frac{1}{2}$ or the two-electron potential E^0 of the acceptor (donor). The rate of electron transfer is influenced by various factors, but in the majority of cases there is a tendency towards its increase with increasing ΔE^1 or E^0 for the acceptor within certain limits. Indeed, $\Delta E \simeq -\Delta G^\circ$ and $\Delta G^* \simeq \Delta G^0$ [see Eqns.(1) and (2)].

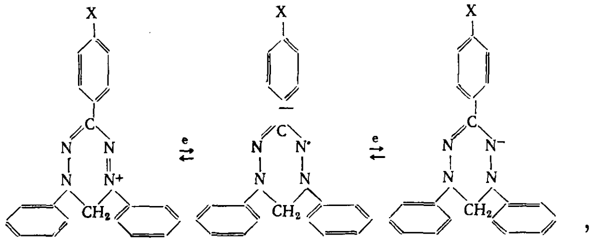
Electron transfer takes place in the acceptor molecule which has a higher (more positive) potential. Many of the so called "cascade" electron transfer processes can be accounted for on the basis of the differences between the oxidation-reduction potentials of donors and acceptors. An interesting example of the cascade electron transfer "initiated" by the electron pulse is the system containing isopropyl alcohol, acetone, acetophenone (AP), benzophenone (BP), and *p*-nitroacetophenone (PNAP):[24]

.

Under the experimental conditions, [AP] > [BP] > [PNAP]. It has been shown by kinetic absorption spectroscopy that the process does indeed proceed in the above sequence[24].

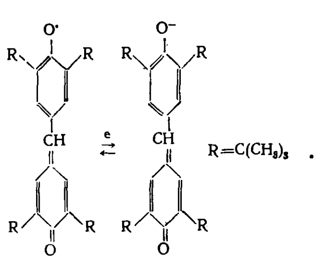
IV. THE POLAROGRAPHY OF FREE RADICALS

Certain stable radicals, for example *C*-phenyl-substituted triphenylverdazyls, are capable of undergoing reversible oxidation or reduction at a dropping mercury electrode[67], which results in one oxidation wave and one reduction wave:



where X = H, Cl, NO_2, CH_3, or OCH_3.

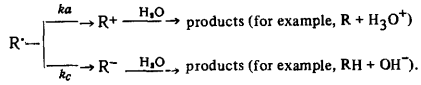
The polarographic reduction of the galvinoxy-radical is also reversible with $E_{1/2}$ = 0.07 V:[68]



.

The polarographic detection of short-lived radicals obtained as a result of an electron pulse has been used in a number of studies[70,71,154]. Such experiments yield oscillograms reflecting the time-dependence of the current. The variation of the concentration of radicals in the bulk of the solution can be investigated in the usual way—by kinetic spectrophotometry. The cathodic and anodic currents give rise to positive and negative signals respectively. The polarograms thus obtained consist of irreversible waves and cannot therefore be used to determine the oxidation-reduction potentials, but they yield valuable information about the behaviour of radicals at the mercury electrode and can be used to identify new radicals formed in the experiments on pulse radiolysis.

In contrast to stable molecules, which can give rise either to an anodic or a cathodic wave (mercury electrode in water, potentials between +0.2 and −1.9 V relative to the calomel electrode), short-lived free radicals usually give rise to both waves in the above potential range. Experiments have shown that the radicals are usually oxidised and reduced at comparable rates in a definite potential range[70]. The oxidation and reduction of radicals may be regarded as competing processes in accordance with the following scheme:



$$R^\cdot \xrightarrow{ka} R^+ \xrightarrow{H_2O} \text{products (for example, } R + H_3O^+)$$
$$R^\cdot \xrightarrow[kc]{} R^- \xrightarrow{H_2O} \text{products (for example, } RH + OH^-).$$

The majority of the waves obtained are completely irreversible, since the oxidation or reduction products of many radicals (such as carbonium ions or carbanions) rapidly react with water before the reverse reaction can take place at the electrode.

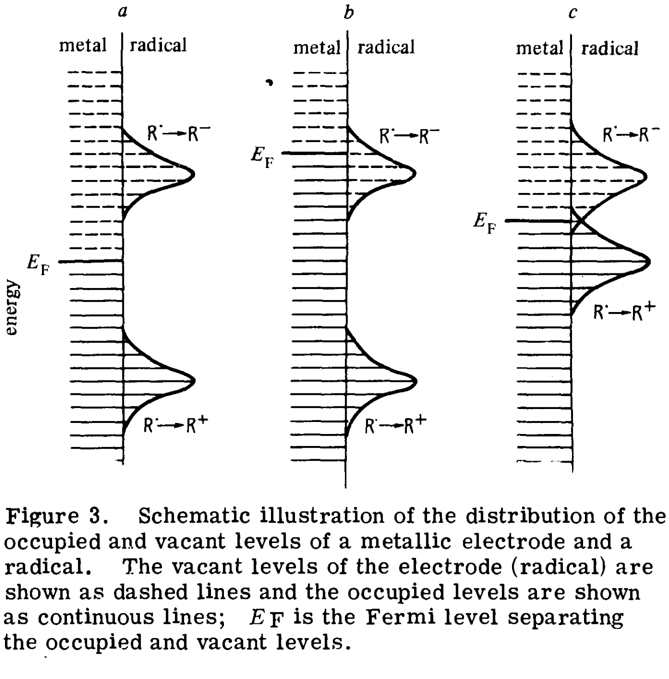


Figure 3. Schematic illustration of the distribution of the occupied and vacant levels of a metallic electrode and a radical. The vacant levels of the electrode (radical) are shown as dashed lines and the occupied levels are shown as continuous lines; E_F is the Fermi level separating the occupied and vacant levels.

The oxidation and reduction of radicals at the electrode can be considered in terms of the scheme illustrated in Fig. 3.[70] Electron transfer can take place only between levels with identical electrode energies in the following system: $R^\cdot \rightarrow R^-$ (reduction) or $R^\cdot \rightarrow R^+$ (oxidation). Thus, according to this scheme, there is neither oxidation nor reduction of $R^\cdot$ in case *a*. With increase of the electrode potential, the energy of the occupied levels increases. Fig. 3*b* illustrates the situation where the reduction of $R^\cdot$ should occur. (The situation where $R^\cdot$ is oxidised may be represented analogously—for this to occur, the value of E_{ph} must be fairly low.) In the case represented in Fig. 3*c* both oxidation and reduction can take place at comparable rates.

A polarographic study of $CO_3^{\overline{\cdot}}$ confirmed the ability of this radical-anion to participate in both oxidation and reduction reactions; it has been established that $E^1(CO_3^{\overline{\cdot}}|CO_3^{2-}) > E^1(CO_3|CO_3^{\overline{\cdot}})$.[158] The study of the polarograms of radicals has made possible definite conclusions about their structures[70].

V. THE $R^{\cdot} + R^{\cdot} \rightarrow$ PRODUCTS REACTION: RECOMBINATION, DISPROPORTIONATION, OR ELECTRON TRANSFER?

It was shown above (Sections II–IV) that free radicals are capable of being both reduced and oxidised in reactions with stable species. Presumably, when two radicals differing in their oxidation-reduction potentials react, electron transfer will again occur. This hypothesis was put forward by Hayon and coworkers[62] on the basis of a study of the oxidation-reduction potentials of short-lived radicals. Indeed, if the radical $^{\cdot}R_2H$ in the reaction

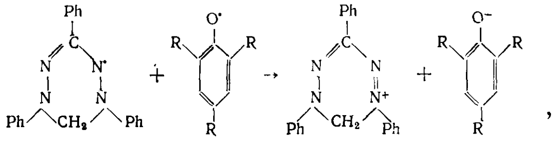
$$^{\cdot}R_1H + {}^{\cdot}R_2H \rightarrow R_1 + R_2H_2$$

has a more positive potential, then, according to the ideas developed above (Section III), one may expect electron transfer from $^{\cdot}R_1H$ to $^{\cdot}R_2H$.[62] The final reaction products will be the same as in the generally accepted mechanism of radical disproportionation (via H atom transfer).

Pokhodenko and coworkers[73–75] observed one-electron transfer in reactions between many stable free radicals:

$$R_1^{\cdot} + R_2^{\overline{\cdot}} \rightarrow R_1^{+} + R_2^{-} \quad , \qquad (31)$$

where, for example, $R_1^{\cdot}$ = triphenylverdazyl and $R_2^{\cdot}$ = 2,4,6-tri-t-butylphenoxyl, galvinoxyl, indophenoxyl, etc. The radical of Wurster's blue oxidises certain triphenylverdazyl radicals and is itself oxidised to the corresponding doubly-charged cation by nitroxy-, phenoxy-, and a number of other stable radicals[75]. The reaction products were identified on the basis of their absorption spectra and the reaction kinetics were followed from the time variation of the intensity of the ESR signal of one of the radicals. It was shown that the reaction



$R{=}C(CH_3)_3$, (32)

in chlorobenzene is described by the second-order kinetic equation: $k_{32} = 8 \times 10^8 \exp(-16\,300 \pm 500)/RT)$ litre mole^{-1} s^{-1}.[73]

Evidently a significant charge separation takes place in the transition states of reactions (31) and (32), so that k_{32} increases with increasing polarity of the medium[73]. The generation of an e.m.f. in electron transfer reactions between two stable free radicals has also been observed[74].

The radical-anions of sulphoanthraquinones ($AQ^{\overline{\cdot}}$) react with the 4-hydroxy-2,2,6,6-tetramethylpyridino-1-oxy-radical ($RNO^{\cdot}$) via electron transfer[57]:

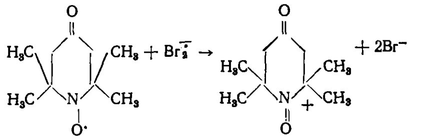
$$AQ^{\overline{\cdot}} + RNO^{\cdot} \rightarrow AQ + RNO^{\overline{\cdot}} \quad .$$

Reaction (32) has a high activation energy and is comparatively slow at room temperature. It is of interest to elucidate the possibility of the occurrence of electron transfer steps in rapid reactions of short-lived radicals with stable radicals or with one another. The stable nitroxy-radical 2,2,6,6-tetramethyl-4-oxopiperidino-1-oxyl (TAN) ($AP^{\cdot}$) reacts with a wide variety of organic and inorganic radicals[76,155]. The rate constants for these reactions are close to the diffusional values. It is not clear whether these reactions involve addition or electron transfer or whether both pathways are involved in competition[76,155]:

$$R^{\cdot} + AP^{\cdot} \rightarrow R - AP \quad , \qquad (33)$$

$$R^{\cdot} + AP^{\cdot} \rightarrow R^{+} + AP^{-} \; (R^{-} + AP^{+}) \quad . \qquad (34)$$

However, it can be regarded as proved that the fast reaction



(35)

involves electron transfer with $k_{35} = 1.6 \times 10^9$ litre mole^{-1} s^{-1}.[76] Indirect evidence has been obtained[73] that the reaction between the active acetyl radical and the triphenylverdazyl radical also involves electron transfer:

$$>N^{\cdot} + CH_3COO^{\cdot} \rightarrow \; >N^{+} + CH_3COO^{-} \quad .$$

The fast reaction of the radical-anion of anthraquinone-2,6-disulphonic acid ($A^{\overline{\cdot}}$) with the $NO_3^{\cdot}$ radical proceeds via the same mechanism[77]:

$$A^{\overline{\cdot}} + NO_3^{\cdot} \rightarrow A + NO_3^{-} \quad , \qquad (36)$$

$$k_{36} = 1.0 \cdot 10^8 \text{ litre mole}^{-1} \text{ s}^{-1}.$$

There is at present no convincing evidence showing that the reactions of uncharged short-lived radicals with one another involve electron transfer. However, hypotheses of this kind have been put forward in a number of studies[62,69,70,148,154]. Radicals capable of being both reduced and oxidised with equal case should have overlapping levels[70] (Fig. 3*c*, Section IV). It can be assumed that such radicals may be destroyed as a result of the formation of ion pairs on collision in solution[70]:

$$R^{\cdot} + R^{\cdot} \rightarrow R^{+} + R^{-} \quad .$$

This process should probably be regarded as involved in competition with the usual radical destruction reactions—recombination and disproportionation via the transfer of a hydrogen atom. For example, the destruction of hydroxycyclohexadienyl radicals can be represented as follows[154]:

$$\begin{array}{l} ^{\cdot}C_6H_6OH + {}^{\cdot}C_6H_6OH \rightarrow \underset{\displaystyle C_6H_5OH + H^{+}}{\underset{\downarrow}{C_6H_6OH^{+}}} + \underset{\displaystyle C_6H_6 + OH^{-}}{\underset{\downarrow}{C_6H_6OH^{-}}} \quad . \end{array} \qquad (37)$$

The detection among the products of reactions between two $R^{\cdot}$ species of compounds whose formation via recombination or disproportions cannot be postulated [for example, C_6H_6 in reaction (37)] would constitute evidence in support of one-electron transfer. The solvent may influence the rate of reaction between two $R^{\cdot}$ species in the manner predicted by the electron transfer theory; such data must be regarded as indirect evidence for electron transfer.

It is well known that alkyl radicals recombine with formation of a new chemical bond between carbon atoms having an unpaired electron:

$$RCH_2CH_2^{\cdot} + R'CH_2CH_2^{\cdot} \rightarrow R\,(CH_2)_4R' \qquad (38)$$

(in the special case where $R = R'$). The rates of the majority of these reactions are limited by diffusion and their activation energies are close to zero[78]. If one of the radicals has an H atom in the β-position relative to the radical centre, there is a possibility of a competing disproportionation reaction[78]:

$$RCH_2CH_2^{\cdot} + R'CH_2CH_2^{\cdot} \rightarrow RCH_2CH_3 + R'CH{=}CH_2 \quad . \qquad (39)$$

Reaction (39) is also diffusion-controlled[78]. The recombination (disproportionation) of such radicals via electron transfer is apparently impossible. In contrast to reactions (38) and (39), the electron transfer reaction

$$RCH_2CH_2^{\cdot} + R'CH_2CH_2^{\cdot} \rightarrow RCH_2CH_2^{+} + R'CH_2CH_2^{-} - \begin{cases} \rightarrow R(CH_2)_4R' \\ \rightarrow RCH_2CH_3 + R'CH{=}CH_2 \end{cases} \qquad (40)$$

requires an activation energy ΔG^* [Eqn.(1)] and in addition the formation of a carbonium ion and a carbanion is a highly endothermic process.

On the other hand, many long-lived or stable radicals with different E^1 values cannot participate in recombination (disproportionation) reactions and are converted into diamagnetic products via electron transfer [reaction (31)]. One can probably postulate that there exists an "intermediate" class of radicals for which ΔG^* [Eqn.(1)] is comparable to $\Delta G^{\neq}$ for recombination (disproportionation) reactions and the radical destruction reaction is in fact reaction (40) involved in competition with reactions (38) and (39).

The reaction

$$R^{\cdot} + R^{\cdot} \rightarrow \text{products} \qquad (41)$$

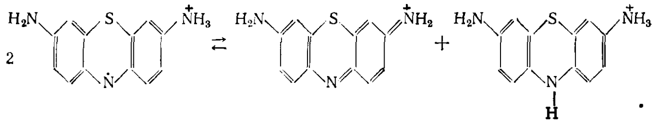
is one of the fundamental processes in the chemistry of short-lived radicals. If it is indeed found that certain radical destruction reactions proceed via electron transfer (the rate-limiting stage), then the kinetics and mechanisms of these reactions in different solvents have to be described in terms of the concepts developed for electron transfer reactions (Section II).

Reaction (41) involves electron transfer if the $R^{\cdot}$ species are radical-ions. Examples of these reactions are the disproportionation of the radical-anions of quinones (Q) or aromatic molecules (Ar):

$$Q^{\overline{\cdot}} + Q^{\overline{\cdot}} \rightleftarrows Q^{2-} + Q \quad ,$$

$$Ar^{\overline{\cdot}},\ M^+ + Ar^{\overline{\cdot}},\ M^+ \rightleftarrows Ar^{2-},\ 2M^+ + Ar \quad .$$

Radical-cations also disproportionate in solutions, for example[79]:



Rapid electron transfer reactions between radical-cations and radical-anions,

$$R_1^{\overline{\cdot}} + R_2^{\overset{+}{\cdot}} \rightarrow R_1^{\cdot} + R_2 + h\nu \quad ,$$

are frequently accompanied by chemiluminescence.

It is noteworthy that rotational diffusion, leading to the mutual orientation of the reactants in the solvent cage required for the occurrence of their reaction, should apparently play a smaller role in bimolecular reactions involving the destruction of radical-ions than in the reactions where uncharged radicals are destroyed[78,79]. This can be understood if account is taken of the fact that the electron transfer takes place over fairly long distances (see Section II, subsection 5).

VI. REACTIONS OF RADICALS WITH METAL COMPOUNDS

Different classes of organic compounds can undergo chemical transformations via a free-radical mechanism in the presence of transition metal compounds. Examples of such processes are the decomposition of peroxides, the halogenation of aliphatic compounds, the amination of aromatic compounds, certain cyclisation reactions, and other processes catalysed by transition metal compounds. Many photochemical reactions of complex compounds lead to the formation of free radicals, which are then involved in dark reactions with metal compounds. In a general form, one can postulate that the interaction of a radical with a metal compound proceeds via one (or several simultaneously) of the following pathways[80,168]:

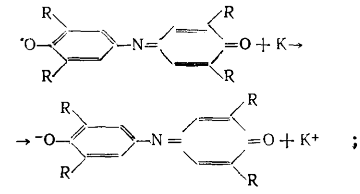
$$R^{\cdot} + M^{n+}L_m - \begin{cases} \rightarrow RH + L'M^{n+}L_{m-1} & \text{(abstraction of hydrogen),} \\ \rightarrow RL + M^{n-1}L_{m-1} & \text{(ligand transfer),} \\ \rightarrow R^{\pm} + M^{(n\mp1)+}L_m\ (M^{n+}L^{\mp}L_{m-1}) & \text{(electron transfer),} \\ \rightarrow {}^{\cdot}RM^{n+}L_{m-1} + L & \text{(ligand substitution),} \\ \rightarrow R^{\cdot}\ldots M^{n+}L_m & \text{(formation of charge-transfer complexes).} \end{cases}$$

Examples of these reactions and the rules that they obey are discussed below.

The influence of transition metal compounds on many organic reactions with radical mechanisms is discussed in a number of reviews[11,81,101,168] and a monograph[82]. Since the publication of the review[83] devoted to the kinetics of the reactions of radicals with metal compounds, many new data have become available.

1. Oxidation-reduction Reactions of Radicals with Metals and Their Compounds

Alkali metals, which are powerful reductants, are capable of reducing various organic species, including free radicals. The indophenoxy- and galvinoxy-radicals react with metallic potassium and are converted into the corresponding phenoxide anions[85,103]:

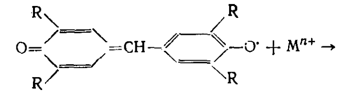


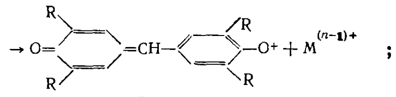
R = C (CH₃)₃ .

Aromatic radical-anions are reduced to the corresponding dianions[87]:

$$Ar^{\overline{\cdot}},\ K^+ + K \rightarrow Ar^{2-},\ 2K^+ .$$

Apart from electron-accepting properties, stable phenoxy-radicals can exhibit the properties of electron donors. 2,4,6-Tri-t-butylphenoxy-, galvinoxy, and indophenoxy-radicals undergo one-electron oxidation in the presence of Lewis acids $MHal_n$ ($M = Sb^V$, Nb^V, Ti^{IV}, Sn^{IV}, or Al^{III}; Hal = Cl or Br), as well as $VOCl_3$ and $AgClO_4$ in various solvents. For example:





$$R = C(CH_3)_3 \ . \qquad (42)$$

The occurrence of reactions of this kind has been demonstrated convincingly by ESR, NMR, spectrophotometric, and polarographic methods[88,89]. The stability of the diamagnetic salts obtained in reactions (42) depends on the structure of the radicals being oxidised, the nature of the oxidant, and the medium. The rate of reaction (42) is described by a second-order kinetic equation: $k_{42} \simeq 10-10^3$ litre $mole^{-1}$ s^{-1} for different $NHal_n$. The study of the interaction of 2,2,6,6-tetramethyl-4-oxopiperidino-1-oxy-radical and DPPH with Group III metal halides showed that the nitroxy-radicals form a complex with $MHal_3$ while DPPH is oxidised to the corresponding cation[89-91]. The results permit the conclusion that the electron-donating properties of the radicals in many respects determine the kinetic parameters of the reaction of stable radicals with $MHal_3$. When the galvinoxy-radical is converted into DPPH, the activation energy of the type (42) reaction increases, owing to the weaker electron-donating properties of DPPH ($E_{1/2} > 0.5$ V) compared with the galvinoxy-radical ($E_{1/2} = 0.38$ V). The nitroxy-radical has a higher oxidation potential ($E_{1/2} \simeq 0.9$ V) and the reaction stops in this instance at the stage involving the formation of the complex[89-91].

A classical example of the manifestation of the electron-donating capacity of free radicals is the reduction of heavy metal salts by the triphenylmethyl radical[92]:

$$Ph_3C^{\cdot} + AgClO_4 \rightarrow Ph_3C^{+}ClO_4^{-} + Ag \ .$$

The oxidation of organic compounds via a radical process in the presence of metal ions has been investigated in the course of eight decades with the aid of Fenton's reagent; this involves the following fundamental processes[93]:

$$H_2O_2 + Fe^{2+} \rightarrow Fe^{3+} + OH^- + OH^{\cdot} \ , \qquad (43)$$

$$HO^{\cdot} + Fe^{2+} \rightarrow Fe^{3+} + OH^- \ , \qquad (44)$$

$$HO^{\cdot} + RH \rightarrow H_2O + R^{\cdot} \ . \qquad (45)$$

The radicals formed participate in the destruction reaction

$$R^{\cdot} + R^{\cdot} \rightarrow \text{products}, \qquad (46)$$

and can regenerate Fe^{2+} or be reduced, oxidising Fe^{2+} at the same time:

$$R^{\cdot} + Fe^{3+} \rightarrow Fe^{2+} + \text{products} \qquad (47)$$

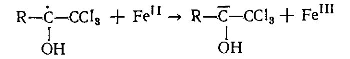
$$R^{\cdot} + Fe^{2+} \xrightarrow{+H^+} Fe^{3+} + RH \ . \qquad (48)$$

Apart from Fenton's reagent, other $H_2O_2 + M^{n+}$ systems are used to generate radicals (see subsection 3 of this section).

In later investigations organic radicals were generated in different systems by pulse radiolysis or by a flow technique, the radicals being identified on the basis of their ESR spectra[95]. Here the active reactant is $OH^{\cdot}$, obtained in the radiolysis of water (pulse radiolysis[66]) or on decomposition of H_2O_2 (using a flow technique).

The data accumulated make it possible to classify radicals in terms of their capacity to participate in oxidation-reduction reactions. The radicals forming comparatively stable carbonium ions oxidise iron(III) effectively and quantitatively [reaction (47)]. They include radicals containing an OH or OR group, amide nitrogen, and tertiary alkyl substituents in the α-position. Primary and secondary alkyl radicals are inert in relation to iron(III), while allyl and benzyl radicals occupy an intermediate position. All these species effectively oxidise copper(II).[93]

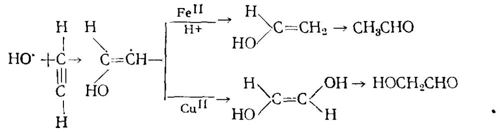
Conjugated carbonyl radicals and related radicals giving rise to comparatively stable anions are inert with respect to oxidation by copper(II) or iron(III). They are readily reduced by iron(II) [reaction (48)], for example[96]:



$$R-\dot{C}(OH)-CCl_3 + Fe^{II} \rightarrow R-\bar{C}(OH)-CCl_3 + Fe^{III} \ .$$

Furthermore, iron(II) reduces the radicals derived from carboxylic acids with a free valence in the α-position, for example $R(R')\mathring{C}CO_2H$, $\dot{C}H_2CO_2H$, and $\dot{C}H(CO_2H)_2$.[97]

Radicals derived from alcohols and carboxylic acids show the opposite tendencies in their capacity to oxidise or reduce iron ions. It has been shown[97] that the ability of hydroxyacid radicals $\dot{R}(OH)CO_2H$ to participate in oxidation-reduction reactions with iron ions is determined by the OH group and not the CO_2H group. Vinyl radicals, obtained as a result of attack by hydroxy-radicals on acetylene, are unique in the sense that they are capable of being both oxidised by copper (II) [but not by iron(III)] and of being reduced by iron(II).[93] Thus acetylene is converted by Fenton's reagent into acetaldehyde in the absence of copper(II) and into hydroxyacetaldehyde in the presence of copper(II):



The oxidation of iron(II) proceeds selectively and the efficiency of the oxidation varies in parallel with the stabilities of the carbonium ions obtained[93].

The iron(III)–EDTA system oxidises different radicals obtained on radiolysis of alcohols, aldehydes, ketones, and dicarboxylic acids[98]. The principal factor influencing the ability of the radical to be oxidised is its structure. Radicals with an unpaired electron in the α-position relative to the functional group as well as radicals without functional groups which would prevent the attainment of the necessary mutual orientation of iron(III) and the reaction centre of the radical are oxidised by iron(III). The oxidation can be very rapid; for example, $k_{47} > 4 \times 10^8$ litre $mole^{-1}$ s^{-1} has been estimated for $\dot{C}H_2OH$.[93] In contrast to this, the ligand exchange reactions of iron(III) have rate constants $k < 10^4$ litre $mole^{-1}$ s^{-1}. These two findings thus agree with an outer-sphere electron transfer mechanism involving the formation of a product of the carbonium ion type:

$$R^{\cdot} + Fe^{III} \rightleftarrows R^{+} + Fe^{II} \ . \qquad (49)$$

Primary and secondary alkyl radicals are not oxidised, probably because in this case equilibrium (49) is displaced to the left[96,99].

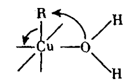
The reduction of many organic radicals by iron(II) is also a very rapid process with $k \geqslant 10^7$ litre $mole^{-1}$ s^{-1} [100] and proceeds more effectively the greater the stability of the resulting carbanion, which also indicates an outer-sphere electron transfer mechanism[93]:

$$Fe^{II} + R^{\cdot} \rightleftarrows Fe^{III} + R^{-} \ .$$

Iron(II) is oxidised by disulphide radical-cations[137]:

$$Fe^{II} + RSSR^{\dot{+}} \rightarrow Fe^{III} + RSSR \ .$$

As stated above, reaction (47) is reversible for primary and secondary alkyl radicals. One can therefore postulate that copper(II), the weakest oxidising agent, cannot oxidise these radicals via an outer-sphere mechanism. It has been shown[93,101] that the radicals are oxidised with formation of an intermediate organocopper compound, which decomposes into hydroxylated products and copper(I):



Oxidation with the aid of copper(II) is usually slower than oxidation by iron(III).[93] The oxidation rate constants for alkyl radicals are $k \simeq 10^6-10^8$ litre mole^{-1} s^{-1},[102] and ligand substitution in the coordination sphere of copper then proceeds fairly rapidly (the bimolecular rate constants are $k \simeq 10^9-10^{10}$ litre mole^{-1} s^{-1}). Consequently the rate-limiting stage in these inner-sphere reactions is electron transfer (see Section II, subsection 1).

It is noteworthy that copper(II) is in general highly reactive in relation to free radicals[11,53,66,94,101,102,104]. Copper(I) compounds can be readily oxidised to copper(II) in their turn. These properties apparently constitute the explanation of the wide-scale employment of copper compounds as catalysts in reactions involving free radicals. Cu^{2+} ions effectively oxidise certain aromatic radicals—chloranil radical-anions ($CQ^{\overline{\cdot}}$), anthraquinone-2,6-disulphonic acid radical-anions ($AQ^{\overline{\cdot}}$), and 2-hydroxy-1-naphthoxy-radicals [Nf(OH)O$^{\cdot}$]:

$$CQ^{\overline{\cdot}} + Cu^{2+} \rightarrow CQ + Cu^{+};\ k = 1{,}0\cdot 10^{9}\ \text{litre mole}^{-1}\ \text{s}^{-1}$$

(in a 9:1 mixture of propanol and water by volume)[80],

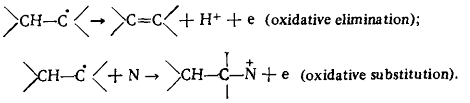
$$AQ^{\overline{\cdot}} + Cu^{2+} \rightarrow AQ + Cu^{+};\ k = 1{,}0\cdot 10^{6}\ \text{litre mole}^{-1}\ \text{s}^{-1}$$

(in water)[140],

$$\text{Nf (OH)O}^{\cdot} + Cu^{2+} \rightarrow \text{products};\ k = (3{,}2 \pm 0{,}6)\cdot 10^{6}\ \text{litre mole}^{-1}\ \text{s}^{-1}$$

(in water)[141].

The oxidation of alkyl radicals by many transition metal compounds in solution leads to the formation of olefins and alkyl derivatives[102]. The following mechanisms may be postulated for these reactions:



$$>CH-\dot{C}< \rightarrow >C=C< + H^+ + e\ \text{(oxidative elimination)};$$

$$>CH-\dot{C}< + N \rightarrow >CH-\underset{|}{\overset{|}{C}}-\overset{+}{N} + e\ \text{(oxidative substitution)}.$$

Here N is a nucleophile (HOAc, HOR, CH_3CN, ArH, etc.);

$$M^{n+}(OAc^-)_n + e \rightarrow M^{(n-1)+}(OAc^-)_n\ \text{(reduction of metal compound)}.$$

The rates of oxidation of n-butyl, isopropyl, and neopentyl radicals by a copper(II) carboxylate have been determined in acetonitrile–acetic acid mixtures[102]. The neopentyl radical is oxidised much more slowly than the other alkyl radicals. An alkylcopper compound is also postulated as an intermediate[102]:

$$(CH_3)_3C\dot{C}H_2 + Cu^{II} \rightleftarrows [(CH_3)_3CCH_2Cu]\ ,$$
$$[(CH_3)_3CCH_2Cu] \rightarrow Cu^{I} + (CH_3)_3CCH_2^{+}\ .$$

Whereas iron(II) ions are capable of reducing only radicals forming comparatively stable anions, titanium(III) ions reduce a wide variety of radicals—alkyl and hydroxyalkyl radicals, radicals derived from carboxylic acids, etc.[97] The reaction

$$Ti^{III} + \dot{C}H\,(COOH)_2 \rightarrow \text{products}\ (Ti^{IV}) \qquad (50)$$

was investigated by ESR combined with radiolysis *in situ*: $k_{50} = 8 \times 10^6$ litre mole^{-1} s^{-1}.[97] The authors[97] believe that the mechanism of this reaction is similar to that adopted for the reduction of hydrogen atoms by iron(II), which includes the formation of a metal hydride intermediate:

$$Fe^{II} + H^{\cdot} \rightarrow Fe^{II} - H^{\cdot}\ ,$$
$$Fe^{II} - H^{\cdot} + H^{+} \rightarrow Fe^{III} + H_2\ .$$

This mechanism can be adopted for the reduction of radicals with an unpaired electron at the carbon atom:

$$R^{\cdot} + M^{n+} \rightarrow M^{n+} - R\ ,$$
$$M^{n+} - R + H^{+} \rightarrow M^{(n+1)+} + RH\ .$$

These are apparently inner-sphere reactions[97,105].

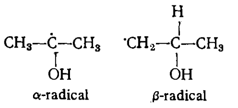
Titanium(III) ions oxidise formic acid radicals[106]:

$$^{\cdot}CO_2H + Ti^{III} - Ti^{II} + CO_2 + H^{+} \qquad (51)$$

with $k_{51} \simeq 5 \times 10^6$ litre mole^{-1} s^{-1}. One may claim (see Section III) that the rate constant for the interaction of the radical-anion with titanium(III) is still greater. Comparison of the rate of substitution by ligands in the coordination sphere of titanium(III) with the rate of reaction (51) suggests that the reaction with titanium(III) proceeds via an outer-sphere mechanism[106].

Europium(III) ions also oxidise $^{\cdot}CO_2H$ and $CO_2^{\overline{\cdot}}$; the rate constant is $k > 7 \times 10^6$ litre mole^{-1} s^{-1}. The reaction does not proceed with ytterbium(III), chromium(III), and scandium(III). It follows from a comparison of the standard oxidation-reduction potentials that chromium(III) is most readily reducible. However, the outer-sphere conversion of chromium(III) into chromium(II) requires a large reorganisation energy in view of the presence of tetragonal distortions in the high-spin chromium(II) complex. The inner-sphere reaction is ruled out in view of the inertness of chromium(III) in relation to substitution[106].

The ability of radicals to participate in oxidation-reduction reactions with metal compounds depends significantly on the structure of the radicals. For example, the α-radical of isopropyl alcohol is oxidised by titanium(IV), iron(III), and chromium(III) more effectively than the β-radical[107]:



$$CH_3-\underset{OH}{\dot{C}}-CH_3 \qquad {}^{\cdot}CH_2-\underset{OH}{\overset{H}{C}}-CH_3$$

because the carbonium ion corresponding to the α-radical is more stable (see Section II, subsection 2).

The inorganic radical-anions $Cl_2^{\overline{\cdot}}$ and $Br_2^{\overline{\cdot}}$ oxidise Fe^{2+}, Co^{2+}, and Mn^{2+} ions[13,108,109]. The reactions were investigated by flash photolysis. The reaction

$$Cl_2^{\overline{\cdot}} + Fe^{2+} \rightarrow Fe^{3+} + 2Cl^{-} \qquad (52)$$

proceeds via an outer-sphere mechanism with $k_{52} = (1.0 \pm 0.2) \times 10^7$ litre mole^{-1} s^{-1}. The inner-sphere reaction

$$Cl_2^{\overline{\cdot}} + Fe^{2+} \rightarrow FeCl^{2+} + Cl^{-} \qquad (53)$$

has a smaller rate constant: $k_{53} = (4.0 \pm 0.6) \times 10^6$ litre mole^{-1} s^{-1}.[13]

The oxidation of $Cl_2^{\overline{\cdot}}$ and $Br_2^{\overline{\cdot}}$ by Mn^{2+} ions takes place with formation of an intermediate complex, which then decomposes into products[109]. The rate-limiting stage in this inner-sphere reaction is electron transfer. The oxidation of Fe^{2+} by the $Br_2^{\overline{\cdot}}$ radical-anion and of Co^{2+} by $Cl_2^{\overline{\cdot}}$ also proceeds via an inner-sphere mechanism, the rate-limiting stage being the substitution reaction[13,108]. The second-order rate constants have been obtained for all the inner-sphere reactions: $k = 10^6$ litre mole^{-1} s^{-1} [13,108,109].

The $N_3^{\overset{\cdot}{-}}$ radical-anion oxidises Fe^{2+} via an inner-sphere mechanism

$$N_3^{\cdot} + Fe^{2+} \rightarrow Fe^{III} + N_3^-$$

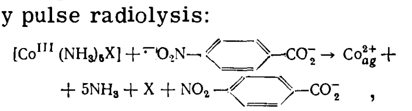
with $k > 1.7 \times 10^9$ litre mole^{-1} s^{-1}.[156]

The reduction of $OH^{\cdot}$ by Fe^{2+} ions has been investigated by pulse radiolysis[110] and it has been established that the reaction proceeds as an outer-sphere electron transfer:

$$OH^{\cdot} + Fe^{2+}(H_2O)_6 \rightarrow Fe^{3+}(H_2O)_6, OH^- \xrightarrow{H^+} Fe^{3+}(H_2O)_6 + H_2O \qquad (54)$$

with $k_{54} = (2.3 \pm 0.2) \times 10^8$ litre mole^{-1} s^{-1}.[110] The corresponding reaction of $OD^{\cdot}$ radicals in D_2O is characterised by the rate constant $k_{54} = (9.4 \pm 0.8) \times 10^7$ litre mole^{-1} s^{-1}. The difference between the rates of these reactions is due to the difference between the free energies of hydration of the ions in the solvents[110]. Many other oxidation-reduction reactions of the $OH^{\cdot}$ radical have been examined[83,169].

The reaction between pentammine(ligand)cobalt(III) complexes and the *p*-nitrobenzoate radical-anion has been investigated by pulse radiolysis:



(55)

where X = NH_3, $PhCO_2^-$, *p*-$O_2NC_6H_4CO_2^-$, Br^-, pyridine, or *m*-$H_2NCOC_5H_4N$. The reaction proceeds via an outer-sphere mechanism in all cases with $k_{55} \simeq 10^6-10^7$ litre mole^{-1} s^{-1}. The reactants initially form an outer-sphere ion pair (they approach one another to a distance equal to the reaction radius) and then electron transfer takes place:

$$\begin{aligned}&[Co^{III}(NH_3)_5X] + {}^-O_2CC_6H_4NO_2^{\overset{\cdot}{-}}\text{-}n \rightleftarrows \\ &\rightleftarrows [Co^{III}(NH_3)_5X, {}^-O_2CC_6H_4NO_2^{\overset{\cdot}{-}}\text{-}n] \xrightarrow{k_{56}} \\ &\rightarrow Co^{2+}_{aq} + 5NH_3 + p\text{-}O_2NC_6H_4CO_2^- + X \quad . \qquad (56)\end{aligned}$$

The intramolecular electron transfer reaction

$$[Co^{III}(NH_3)_5(O_2CC_6H_4NO_2\text{-}n)]^+ \rightarrow Co^{2+}_{aq} + 5NH_3 + p\text{-}O_2NC_6H_4CO_2^- \qquad (57)$$

was found to have $k_{57} = 2.6 \times 10^3$ s^{-1} with $k_{57} < k_{56}$, i.e. the intramolecular transfer is slower. The most probable explanation of this is that the carboxylate ion exhibits a comparatively low "electron permeability"[111].

The rate constants for reactions with participation of *m*- and *o*-nitrobenzoate radical-anions, analogous to reaction (57), are 1.5×10^2 and 4.0×10^5 s^{-1} respectively[112,166]. The increase of the rate of reaction by several orders of magnitude for the ortho-isomer is probably due to the overlapping of the orbitals of the nitro- and carboxy-groups, which generates an effective pathway for electron transfer. The study of the distribution of spin density in the radical helps to interpret the kinetic data[166].

The strong reductant $CO_2^{\overset{\cdot}{-}}$ is oxidised by various cobalt(III) complexes[111]:

$$CO_2^{\overset{\cdot}{-}} + Co^{III}(NH_3)_5X^{2+} \rightarrow CO_2 + \text{reduced complex.} \qquad (58)$$

The reaction has been investigated by pulse radiolysis combined with the method of competition kinetics: $k_{58} = 10^7-10^9$ litre mole^{-1} s^{-1}. The complexes investigated can be divided into two groups: (1) highly reactive complexes whose reactions involve direct attack on the ligand and electron transfer to an available orbital localised at the ligand; (2) complexes exhibiting a moderate reactivity in which ligand orbitals of lower energies are saturated and the available antibonding orbitals have high energies. As in the study of Land and Swallow[113] (see below), no direct correlation was observed between k_{58} and the overall charge of one of the reactants (in the present instance the complex). k_{58} is more influenced by the properties of the complex as a whole than by the properties of any one free ligand X. Nor was a correlation observed between the rate constants for electron transfer from the $CO_2^{\overset{\cdot}{-}}$ and $^{\cdot}CH_2OH$ radical species to the $Co^{III}.(NH_3)_5X^{2+}$ complexes [reaction (58)] and E^0 for the complex. This can be explained by the comparatively low values of E^0 for such complexes (see Section II, subsection 2), which corresponds to a small difference between their free energies. One can then expect that other factors affect the rate constant for the electron transfer reaction[38].

The ions of metals in unusual valence states inhibit or catalyse various chemical reactions. Reactions of Ni^+ ions with radicals have been investigated[114]. The Ni^+ ions and organic radicals were generated by an electron pulse, the intermediates being detected on the basis of the absorption spectra and conductimetrically. It was found that Ni^+ is capable of reducing various radicals extremely effectively and of forming intermediate complexes:

$$Ni^+ + {}^{\cdot}CH_2C(CH_3)_2OH \rightarrow Ni^{2+} + CH_2=C(CH_3)_2 + OH^- ,$$
$$Ni^+ + CO_2^{\overset{\cdot}{-}} \rightarrow NiCO_2 ,$$
$$Ni^+ + {}^{\cdot}CH_2OH \rightarrow NiCH_2OH^+ ,$$
$$Ni^+ + \dot{C}(CH_3)_2OH \rightarrow NiC(CH_3)_2OH^+ .$$

The complexes interact with water:

$$NiCH_2OH^+ + H_2O \rightarrow Ni^{2+} + CH_3OH + OH^-$$

or with another Ni^+ ion, forming metallic nickel

$$Ni^+ + NiC(CH_3)_2OH^+ \rightarrow Ni^{2+} + Ni + (CH_3)_2\dot{C}OH .$$

Pb^{2+} ions oxidise via a one-electron transfer mechanism hydroxyalkyl radicals and the $CO_2^{\overset{\cdot}{-}}$ radical-anion[161]:

$$Pb^{2+} + CO_2^{\overset{\cdot}{-}} \rightarrow Pb^+ + CO_2 ,$$
$$Pb^{2+} + (CH_3)_2\dot{C}OH \rightarrow Pb^+ + (CH_3)_2CO + H^+ .$$

Pb^+ ions may be reduced to metallic lead in reactions with hydroxyalkyl radicals[161]:

$$Pb^+ + (CH_3)_2\dot{C}OH \rightarrow Pb\dot{C}(CH_3)_2OH^+ \rightarrow Pb + H^+ + (CH_3)_2CO .$$

The reaction proceeds via the formation of an intermediate radical-ion complex.

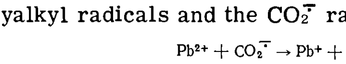
Pb^+ ions are oxidised by the radicals obtained on radiolysis of solutions in t-butyl alcohol and cyclopentane[161]:

$$Pb^+ + {}^{\cdot}CH_2(CH_3)_2COH \rightarrow Pb^{2+} + OH^- + CH_2=C(CH_3)_2 ,$$
$$Pb^+ + C_5H_9^{\cdot} \xrightarrow{H_2O} Pb^{2+} + C_5H_{10} + OH^- .$$

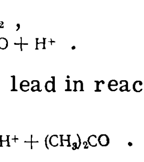
Cytochrome *c* effectively oxidises various radicals:

$$Fe^{III}\ \text{cyt}\ c + R^{n+} \rightarrow R^{(n+1)+} + Fe^{II}\ \text{cyt}\ c \quad . \qquad (59)$$

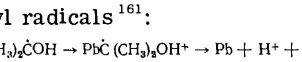
$k_{59} = 2.4 \times 10^8$ litre mole^{-1} s^{-1} for lactic acid radicals[115], $k_{59} = 5 \times 10^8$ litre mole^{-1} s^{-1} for $CO_2^{\overset{\cdot}{-}}$ radical-anions[116], and $k_{59} = 1.8 \times 10^8$ litre mole^{-1} s^{-1} for radicals derived from ethanol[115]. The oxidation of pyridine radicals by cytochrome *c* has been studied by pulse radiolysis[113]. The radicals were obtained by the one-electron reduction of the following bypyridylium and pyridylium compounds:



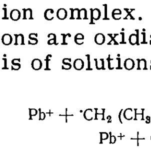
(I)



(II)



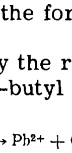
(III)



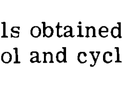
(IV)

NAD^+

(V)



(VI)



(VII)

The resulting rate constants can be divided into two groups. It was found that $k_{59} = (1.8 \pm 0.4) \times 10^8$ litre mole^{-1} s^{-1} for the radical species derived from the bipyridylium salts (I)–(IV) and $k_{59} = (8 \pm 1) \times 10^8$ litre mole^{-1} s^{-1} for the radical species obtained from compounds (V)–(VII).[113] The difference between the values of k_{59} for these groups of radical species may be accounted for by the presence of the positive charge in the radical species from compounds (I)–(IV), which should retard the reaction with the positively charged cytochrome *c*, but this effect is weakened owing to the high ionic strength of the solution. The main reason for the difference may be that the oxidation-reduction potentials of compounds (I) to (IV) are in the range between −0.3 and −0.55 V,[117] while those of compounds (V)–(VII) are in the range between −0.9 and −1.1 V.[113] The reaction apparently proceeds via attack on the part of the porphyrin ring remote from Fe(III), which is confirmed by the high values of k_{59} and resembles the reaction with an organic acceptor rather than with a simple metal complex[41,113].

2. Complexes of Radicals with Transition Metal Compounds

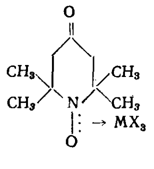
The oxidation-reduction reactions between radicals and metal compounds involving inner- or outer-sphere mechanisms terminate with the decomposition of the intermediate complex or the collision complex into the final products. However, in both cases complexes of the charge-transfer type, association complexes, or coordination compounds with radical ligands may be formed when no oxidation-reduction reactions are observed. Apart from the chemical affinity between the radical and the metal compound, paramagnetic interactions may play an important role in the formation of such complexes, because many metal ions have unfilled or partly filled orbitals, Complexes of radicals and metal compounds (ions) are of great interest, because complex formation alters greatly the reactivity of the radicals. In many cases this entails a relative stabilisation of the radical.

Depending on the degree of charge transfer, the structures of the complexes can be conventionally described by the following formulae:

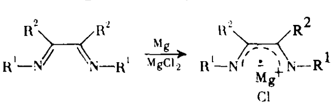
$$R^{\cdot}M^{n+};\quad R^{+}M^{(n-1)+};\quad R^{\overset{\cdot}{-}}M^{(n+1)+}.$$

The metal in complexes of this kind is frequently in an unusual valence stage. The radical ligand has an unpaired electron which is highly delocalised. Under these conditions, the splitting of the ESR spectral lines of the radical, caused by the interaction of the unpaired electron with the paramagnetic metal nucleus, is observed in many instances[66,101]. Despite this, the radical retains its nature in many complexes, which has been confirmed by ESR studies[101].

Stable aliphatic nitroxy-radicals form in solution complexes with aluminium(III) and gallium(III) halides[90,91]. The existence of complexes of the 2,2,6,6-tetramethyl-4-oxopiperidino-1-oxy-radical with the above compound has been demonstrated by ESR. The most probable structure of the complexes is shown below:

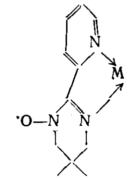


Here the vacant orbital of the Lewis acid interacts with the 3-π-electron fragment N...O, which leads to a slight distortion of the planar configuration of the complex at the nitrogen atom and to an increase of a_N compared with the initial nitroxy-radical[91]. Stable radicals capable of forming complexes with ions having filled electron shells (d^0 or d^{10}) may be obtained by the one-electron reduction of molecules containing the fragments shown below:



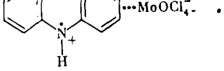
These may be *αα′*-bipyridyl, *o*-phenanthroline, etc. The ESR spectra of a number of such complexes of glyoxal-bis-*N*-t-butylimine (R_1 = t-butyl and R_2 = H) have been recorded[118]. The ESR data have shown that the unpaired electron is delocalised over the entire complex MLCl, including the halogens.

Paramagnetic ligands capable of delocalising the unpaired electron over diamagnetic metal atoms are extremely rare. Complexes of this kind are of interest for the investigation of metal–ligand bonds as well as spin labels linked to the metal ion in proteins. When such labels are employed, spin density is transferred from the radical ligand via the metal to the remaining part of the ligand environment. The stable pyridyliminonitroxy-radical forms complexes with various diamagnetic metal ions[119]:

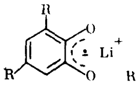


M=Zn^{II}, Cd^{II}, or Hg^{II}.

In certain cases complexes of radicals with metal compounds may be isolated in a crystalline state[120]. The tetrachloro-oxomolybdate of the phenothiazinium radical-cation, isolated in the solid state, gives rise to an ESR spectrum with a single broad signal (g = 1.98), while the ESR spectrum of the complex in solution consists of two superimposed singlets with different g-factors[120]:

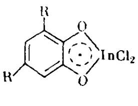


The ions of Groups I–III metals form complex with *o*-quinone radical-anions[121–125]. ESR data have shown that the majority of the complexes remain π-radicals and the degree of transfer of spin density to the metal ion is low[124]. The nature of the oxygen–metal bond has a marked influence on the distribution of the unpaired electron density in the *o*-semiquinone and on the hyperfine interaction with the paramagnetic nucleus of the central atom. Complexes with alkali metal ions, for example, complex (VIII), can be regarded as contact ion pairs:

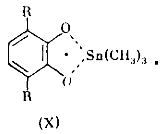


(VIII)

R = C(CH₃)₃

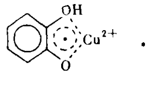


(IX)



(X)

Complexes formed with thallium(I) or indium(III) ions [for example, compound (IX)] are apparently chelates[123]. Significantly higher constants for the hyperfine interaction with metal nuclei compared with contact ion pairs have been obtained from the ESR spectra of the chelates[123]. The ESR spectrum of the tin-containing radical (X), which can be usefully regarded as an organoelemental radical rather than a complex, has been measured[128]. Thus the ESR data for radical complexes make it possible to investigate the nature of the oxygen–metal bond. The complexes of neutral semiquinone radicals having a chelate unit have been recorded by flash photolysis[86]:



The complexes of short-lived radicals with transition metal compounds are destroyed via second-order reactions, like the radicals themselves, but the rate constants are significantly lower than those for the destruction of free radicals. Complexes of the *p*-benzoquinone radical-anion ($Q^{\overline{\cdot}}$) with Cu^{n+} ions have been detected[104]. The rate constants for the reactions

$$Q^{\overline{\cdot}} + Q^{\overline{\cdot}} \xrightarrow{2H^+} Q + QH_2 \qquad (60)$$

$$Q^{\overline{\cdot}}Cu^+ + Q^{\overline{\cdot}}Cu^+ \rightarrow \text{products.} \qquad (61)$$

are $k_{60} = 1.2 \times 10^8$ litre $mole^{-1}$ s^{-1} and $k_{61} = 1.6 \times 10^7$ litre $mole^{-1}$ s^{-1} (in water).

The complex $Pb\dot{C}(CH_3)_2OH^+$, formed by the Pb^+ ion with the α-radicals derived from isopropyl alcohol, has a much longer life in solution than the initial radical[161]. However, the ion pairs involving radical-anions are destroyed faster than the initial radicals. The rate constants for the reactions

$$T^{\overline{\cdot}} + T^{\overline{\cdot}} \rightleftarrows T^{2-} + T \quad , \qquad (62)$$

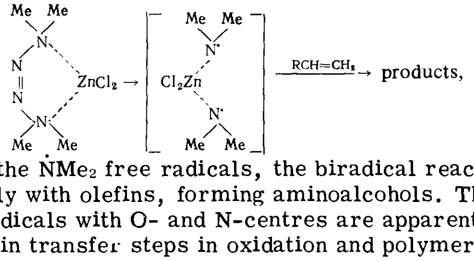
$$T^{\overline{\cdot}}, Na^+ + T^{\overline{\cdot}}, Na^+ \rightleftarrows T^{2-}, 2Na^+ + T \qquad (63)$$

of the tetraphenylethylene (T) radical-anions in tetrahydrofuran (THF) have been estimated: $k_{62} < 10^3$ and $k_{63} < 8 \times 10^6$ litre $mole^{-1}$ s^{-1}.[129] In this case the Coulombic repulsion of the similarly charged species [reaction (62)] has a decisive influence on the kinetics[129]. The rate constant $k_{64} = 1 \times 10^7$ litre $mole^{-1}$ s^{-1} has been obtained for the reaction between the ion pair and the radical:

$$T^{\overline{\cdot}}, Na^+ + T^{\overline{\cdot}} \rightleftarrows T^{2-}, Na^+ + T \ . \qquad (64)$$

Reaction (63) is slower than reaction (64), since two Na^+ ions are desolvated simultaneously in the transition state of reaction (63).[129]

As stated above, the reactivity of the radicals changes markedly on formation of complexes. Evidence has been obtained[130] for the existence of a biradical complex formed on thermal decomposition of the complex of tetramethyl-2-tetrazene with $ZnCl_2$:



In contrast to the $\dot{N}Me_2$ free radicals, the biradical reacts very selectively with olefins, forming aminoalcohols. The coordinated radicals with O- and N-centres are apparently inactive in chain transfer steps in oxidation and polymerisation reactions, which is important in connection with the problem of the inhibiting activity of phenols, aromatic amines, and related compounds[131,132].

The ability of transition metal ions to catalyse the recombination of methyl radicals is explained by the formation of an intermediate species—the complex of the alkyl radical with the metal ion, which is stable in relation to the abstraction of a hydrogen atom and participates only in the reaction with the analogous complex[133]:

$$\dot{C}H_3 + M^{n+} \rightleftarrows {}^{\cdot}CH_3M^{n+} \quad ,$$

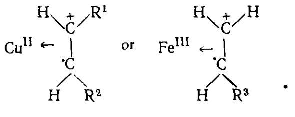
$$2\dot{C}H_3M^{n+} \rightarrow C_2H_6 + 2M^{n+} \quad .$$

Studies by pulse radiolysis have shown that $OH^{\cdot}$ forms a complex with benzoatopentamminecobalt(III),[134] adding to the ligand—the benzoate anion:

$$(NH_3)_5\, Co^{III}\, (O_2CC_6H_5OH)$$

The complex is destroyed via a second-order reaction: $k = 9.3 \times 10^7$ litre $mole^{-1}$ s^{-1}, which is significantly less than the rate constants for the reactions of $OH^{\cdot}$ radicals and their adducts with benzoic acid and benzoate ion (1.2×10^8 and 4.4×10^8 litre $mole^{-1}$ s^{-1} respectively)[134].

When s-butyl-lithium was oxidised with the aid of di-isopropyl salicylate or copper(II) or iron(III) acetylacetonate, ESR spectra were recorded[126]. The absence of splitting by the copper nucleus and the low constants for the hyperfine splitting by protons enabled the authors to attribute the following structure to the complexes:



The unpaired electron is localised in an orbital of the carbon atom[126].

Hyperfine splitting by the silver nucleus has been observed in the ESR spectra of many silver(I)–olefin radical complexes ($g = 2.0017$) formed when polycrystalline silver complexes of olefins are subjected to γ-irradiation[127]. Analogous complexes with a radical ligand have been obtained on irradiating compounds of silver perchlorates with cyclohexa-1,3-diene or cyclohexa-1,4-diene. The constants for hyperfine splitting by the protons in the complex

are virtually the same as in the spectrum of the free cyclohexadienyl radical, which indicates a weak interaction between the hydrocarbon radical and the nucleus of the metal ion[127].

The formation of a complex by the benzyl radical and chromium(II) has been reported[135]:

$$Ph\dot{C}H_2 + Cr^{II} \rightleftarrows Ph\dot{C}H_2Cr^{II} \quad .$$

Complexes of related aromatic radicals—semiquinone and phenoxy-radicals—have been discussed in a review[66].

Many complexes of radicals and transition metal ions (compounds) have structures resembling very closely those of ion pairs formed by aromatic radical-anions and alkali metal ions. The difference consists in the absence of electrostatic attraction which holds together ion pairs[101].

The study of the interaction of peroxy-radicals $R\dot{O}_2$ with transition metal compounds is of interest in connection with the investigation of homogeneous-catalytic liquid-phase oxidation of hydrocarbons. The existence of complexes formed by peroxy-radicals $R\dot{O}_2$ with vanadyl, cobalt, and manganese acetylacetonates and naphthenates has been suggested[136–138]. The studies were performed by the ESR method, solutions of the hydroperoxide ROOH and $M^{n+}L_m$ being mixed. The authors believe that the formation of the complex stabilises $R\dot{O}_2$. However, it is not stated[136-138] whether ROOH has been completely consumed at the time when the ESR spectra of the stabilised $RO_2^{\cdot}$ were observed. If ROOH were present in solution, then fairly high $RO_2^{\cdot}$ concentrations might have been observed for a long time simply owing to the decomposition of the hydroperoxide[139], which throws doubt on the conclusions reached by the authors[136-138].

3. Interactions of the Hydroperoxy-radicals with Metal Ions

Under certain conditions, hydroperoxy-radicals capable of interacting with metal ions are formed in systems of the type of Fenton's reagent. In the presence of an excess of H_2O_2, $HO_2^{\cdot}$ radicals are formed by the reaction[142]

$$Ce^{4+} + H_2O_2 \rightarrow Ce^{3+} + H^+ + HO_2^{\cdot} \qquad (65)$$

or via the reactions[142-144]

$$M^{n+} + H_2O_2 \rightarrow M^{(n+1)+} + OH^- + OH^{\cdot} \;, \qquad (66)$$

$$OH^{\cdot} + H_2O_2 \rightarrow H_2O + HO_2^{\cdot} \;, \qquad (67)$$

$$M^{n+} = Ti^{3+},\; Fe^{2+},\; V^{4+}, \text{ or } Cr^{2+}.$$

The interaction of the hydroperoxy-radical with metal ions was studied on stopped flow apparatus with two mixing chambers: the $HO_2^{\cdot}$ radical was formed in the first chamber via reaction (65) and, when the latter had reached completion, the solution was mixed with the solution of the metal ions in the second chamber. The changes in the system were followed on the basis of the ESR spectra.

The method of flash photolysis with detection of intermediates by ESR is convenient for kinetic measurements. $HO_2^{\cdot}$ radicals are then generated via reaction (67) and

$$H_2O_2 + h\nu \rightarrow 2OH^{\cdot}$$

in a cell located in the cavity of the ESR spectrometer. It is also possible to investigate the reactions of $HO_2^{\cdot}$ radicals by the method of steady-state radiolysis in combination with a flow system and ESR.

The existence of complexes of $HO_2^{\cdot}$ with a number of transition metal ions, such as Ti^{4+}, Zr^{4+}, Ce^{3+}, V^{5+}, Th^{4+}, U^{6+}, Mo^{6+}, etc. has been established[142,145-151]:

$$M + HO_2^{\cdot} \rightleftarrows M{-}HO_2^{\cdot} \quad . \qquad (68)$$

The complexes may be formed not only via reaction (68) but in many instances also as a result of the interaction of the $HO_2^{\cdot}$ or $OH^{\cdot}$ radicals with the $M{-}H_2O_2$ complex[142]:

$$M{-}H_2O_2 + HO_2^{\cdot} \rightarrow M{-}HO_2^{\cdot} + H_2O_2 \quad ,$$

$$M{-}H_2O_2 + OH^{\cdot} \rightarrow M{-}HO_2^{\cdot} + H_2O \quad .$$

In the presence of ions of two metals, M and M′, ESR spectra due to two species have been recorded: $M{-}HO_2^{\cdot}$ and $M'{-}HO_2^{\cdot}$. The occurrence of the reversible reaction[142]

$$M{-}HO_2^{\cdot} + M' \rightleftarrows M'{-}HO_2^{\cdot} + M \qquad (69)$$

was demonstrated. This may be a bimolecular reaction [Eqn. (69)] or it may proceed via the association of the complex $M{-}HO_2^{\cdot}$ [the reverse process in reaction (68)] followed by the formation of the complex with the M′ ion. Reaction (69) involving many pairs of ions has been observed: $U^{6+}{-}Th^{4+}$, $Th^{4+}{-}Zr^{4+}$, $Zr^{4+}{-}U^{6+}$, $Th^{4+}{-}Ti^{4+}$, $U^{6+}{-}Ti^{4+}$, $V^{5+}{-}Ti^{4+}$.[142] Kinetic studies have shown that the exchange reaction between Cu^{2+} and Th^{4+} ions is more likely to proceed via the direct transfer of $HO_2^{\cdot}$ than via a dissociation-association mechanism[145]:

$$Cu^{2+} + [Th{-}HO_2]^{4+} \rightleftarrows [Cu{-}HO_2^{\cdot}]^{2+} + Th^{4+} \;, \qquad (70)$$

where $K_{70} = 3 \times 10^2$.

Apart from the $M{-}HO_2^{\cdot}$ complexes, more involved $M{-}HO_2{-}M'$ complexes may exist[145]. The $HO_2^{\cdot}$ radical disproportionates in solution:

$$HO_2^{\cdot} + HO_2^{\cdot} \rightarrow H_2O_2 + O_2 \qquad (71)$$

with $k_{71} = 6.7 \times 10^5$ litre $mole^{-1}$ s^{-1}.[152] Under the experimental conditions, the lifetime of the $HO_2^{\cdot}{-}M$ complexes is significantly longer than that of $HO_2^{\cdot}$. This is one of the reasons why the ESR spectra of many such complexes have been recorded. The Zr^{4+}, Th^{4+}, and U^{6+} complexes are destroyed via first-order reactions for higher values of [M]. The lifetime of such complexes varies from several tenths of a second to several seconds[142]. The lifetime of the $Nb^{5+}{-}HO_2^{\cdot}$ and $La^{3+}{-}HO_2^{\cdot}$ complexes is significantly shorter, which gives rise to certain difficulties in their detection[146].

Apart from their involvement in complex-formation reactions, the $HO_2^{\cdot}$ and $O_2^{\overline{\cdot}}$ radical species participate in oxidation-reduction reactions. Thus Cu^{2+} oxidises the $HO_2^{\cdot}$ radical[152]:

$$Cu^{2+} + HO_2^{\cdot} \rightarrow Cu^+ + H^+ + O_2 \qquad (72)$$

with $k_{72} \simeq 1 \times 10^8$ litre $mole^{-1}$ s^{-1}. Reaction (72) also proceeds via the formation of a complex[145]:

$$Cu^{2+} + HO_2^{\cdot} \rightleftarrows [Cu{-}HO_2^{\cdot}]^{2+} \;, \qquad (73)$$

$$[Cu{-}HO_2^{\cdot}]^{2+} \rightarrow Cu^+ + H^+ + O_2 \qquad (74)$$

[$K_{73} = (5.1 \pm 1.0) \times 10^7$ litre $mole^{-1}$, and $k_{74} = 30 \pm 5$ s^{-1}] and reaction (74) determines the rate of oxidation for higher values of $[Cu^{2+}]$.

The oxidation of $O_2^{\overline{\cdot}}$ by Cu^{2+} ions also proceeds with formation of an intermediate complex[149,151,152]:

$$Cu^{2+} + O_2^{\overline{\cdot}} \rightarrow [CuO_2]^+ \rightarrow Cu^+ + O_2 \qquad (75)$$

with $k_{75} = (1.7 \pm 0.3) \times 10^9$ litre $mole^{-1}$ s^{-1}¶ [150,151].

It has been found that the complex of $O_2^{\overline{\cdot}}$ and Cu^{2+} exists and that its lifetime is shorter than that of the complex with $HO_2^{\cdot}$.[145,152] This is quite reasonable, since $O_2^{\overline{\cdot}}$ is a stronger reducing agent than $HO_2^{\cdot}$: $E^0_C(O_2|O_2^{\overline{\cdot}}) < E^0_C|HO_2^{\cdot})$ [39] (see Section III). Cu^+ ions reduce $HO_2^{\cdot}$ and $O_2^{\overline{\cdot}}$:[152]

$$Cu^+ + O_2^{\overline{\cdot}} \xrightarrow{2H_2O} Cu^{2+} + H_2O_2 + 2OH^- \;, \qquad (76)$$

$$Cu^+ + HO_2^{\cdot} \xrightarrow{H^+} Cu^{2+} + H_2O_2 \qquad (77)$$

with $k_{76} > 10^9$ litre $mole^{-1}$ s^{-1} and $k_{77} \simeq 10^{10}$ litre $mole^{-1}$ s^{-1}.

In contrast to Cu^{2+} ions, Fe^{3+} ions oxidise $O_2^{\overline{\cdot}}$ via an outer-sphere mechanism:

$$Fe(H_2O)_6^{3+} + O_2^{\overline{\cdot}} \rightarrow Fe(H_2O)_6^{3+},\; O_2^{\overline{\cdot}} \rightarrow Fe^{2+} + O_2 \qquad (78)$$

with $k_{78} = (8 \pm 2) \times 10^8$ litre $mole^{-1}$ s^{-1}.[49,150]

Titanium(IV) and vanadium(V) ions form fairly stable complexes with $O_2^{\overline{\cdot}}$.[149] Analysis of the results of ESR studies of these complexes and the interpretation of the structures of the complexes with the aid of the molecular orbital method have shown that the molecular oxygen in the coordination spheres of these metal ions should have a singlet ground state[149]. This conclusion makes it possible to explain the relative stability of the radical complexes with respect to electron transfer within the inner-sphere. The highest molecular orbitals of $O_2^{\overline{\cdot}}$ are designated by π^* (HOMO) and $\bar{\pi}^*$. The energetically most favourable direct electron transfer $\pi^* \rightarrow t_{2g}$ with formation of singlet oxygen in the coordination sphere is forbidden by symmetry considerations. Electron transfer

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¶ According to Rabani et al.[152], $k_{75} = 8 \times 10^9$ litre $mole^{-1}$ s^{-1}.

from the π orbital to the t_{2g} orbital requires a large activation energy, since it leads to the formation of oxygen in the excited triplet state[149].

The high rate of electron transfer within the inner sphere in the $Cu^{2+}O_2^{\bar{\cdot}}$ complex is apparently caused by the σ-coordination of oxygen[149].

The kinetics and mechanism of the formation and destruction of radical complexes in the titanium(IV)–H_2O_2–cerium(IV) system have been investigated in detail[147] by ESR. The accumulation of the radical $Ti^{IV}O_2^{\bar{\cdot}}$ complex in this system proceeds via the reactions

$$Ti^{IV}(O_2^{2-}) + Ce^{IV} \underset{k_b}{\overset{k_a}{\rightleftarrows}} Ti^{IV}(O_2^{2-})Ce^{IV} \xrightarrow{k_{79}} Ti^{IV}(O_2^{\bar{\cdot}}) + Ce^{III}, \qquad (79)$$

$$k_a = 5 \cdot 10^4 \text{litre mole s}^{-1}, \quad k_b = 130 \text{ s}^{-1}, \quad k_{79} = 75 \text{ s}^{-1}.$$

The $Ti^{IV}O_2^{\bar{\cdot}}$ complex is destroyed via the reactions:

$$Ti^{IV}O_2^{\bar{\cdot}} + Ce^{IV} \rightleftarrows Ti^{IV}(O_2^{\bar{\cdot}})Ce^{IV} \xrightarrow{k_{80}} Ti^{IV} + Ce^{III} + O_2, \qquad (80)$$

$$Ti^{IV}O_2^{\bar{\cdot}} + H^+ \rightleftarrows HO_2^{\cdot} + Ti^{IV}, \qquad (81)$$

$$Ti^{IV}O_2^{\bar{\cdot}} + Ti^{IV}O_2^{\bar{\cdot}} \rightarrow \text{products}, \qquad (82)$$

$$Ti^{IV}O_2^{\bar{\cdot}} + HO_2^{\cdot} \rightarrow \text{products} \qquad (83)$$

$$k_{80} = 7 \text{ s}^{-1}, \quad k_{81} = 2 \text{ litre mole}^{-1}\text{ s}^{-1}, k_{82} \leqslant 500 \text{ litre mole}^{-1}\text{ s}^{-1},$$
$$k_{83} > 2{,}8 \cdot 10^5 \text{ litre mole}^{-1}\text{ s}^{-1}, \quad k_{-81} > 2{,}8 \cdot 10^3 \text{ litre mole}^{-1}\text{ s}^{-1}.$$

The reversible formation of copper(II) complexes of $O_2^{\bar{\cdot}}$ has also been observed in an organic medium[153]. In the oxidation of methanol in an alkaline medium and of cumene, it was observed that the catalytic effect of the copper complexes of *o*-phenanthroline (*o*-P) is due to the formation of the complex $Cu^I(o\text{-}P)_2$ in the system, which coordinates oxygen, forming a copper(II) complex:

$$Cu^I(o\text{-}P)_2 + O_2 \rightleftarrows Cu^{II}(o\text{-}P)_2O_2^{\bar{\cdot}}$$

---o0o---

Thus many reactions involving free radicals proceed via one-electron transfer. Fairly extensive experimental data on the oxidation-reduction reactions of radicals have now accumulated, which makes it possible to establish certain structural-kinetic rules. Kinetic data are very important for the theory of electron transfer and for its further development.

The vast majority of free radicals are short-lived in liquid solutions, which necessitated the use of flow or pulse techniques in order to obtain reliable information about reactions involving them. The use of the pulse radiolysis method proved to be extremely promising for the measurement or estimation of one-electron potentials of free radicals. The knowledge of such potentials permits in the majority of instances a correct prediction of the direction and rate of the oxidation-reduction reaction.

The study of one-electron transfer reactions involving cytochromes, oxygen, quinones, flavins, and pyridine bases is of interest for the elucidation of the detailed mechanism of electron transport in biological systems.

Transition metal compounds are widely used as catalysts in radical reactions. The reactions of macroradicals with transition metal complexes play an important role in radical polymerisation and in the stabilisation of polymers. Different metal complexes or salts can have a significant influence on the kinetics and mechanisms of radical oxidation and reduction reactions of organic compounds.

The study of the influence of the magnetic field on the kinetics of oxidation-reduction reactions of radicals with transition metal compounds having different electronic configurations may promote a further development of the theory of magnetic effects in radical reactions.

The study of coordination compounds with radical ligands constitutes a new field in the chemistry of complex compounds. On formation of the complex with a transition metal compound, the reactivity of the radical changes; in most cases short-lived radicals become more stable on forming a complex.

The oxidation-reduction reactions of free radicals can have a wide variety of practical applications. The electron transfer reactions between certain stable free radicals generate an e.m.f. The one-oxidation of $CO_3^{\bar{\cdot}}$ constitutes the basis of the reduction of oxygen by the action of visible light on the duroquinone–carbonate ion system and thus provides a valuable means of utilising solar energy.

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The Photonics of Porphyrin Molecules

I.I.Dilung and E.I.Kapinus

The review deals with the properties and behaviour of porphyrin molecules in an excited state. Modern data on the electronic structure of metalloporphyrins and their luminescence-spectroscopic properties are presented. The problems of the photonics of metalloporphyrins, which are of great importance for the understanding of the initial stages in photosynthesis and for the control of the latter, are discussed in detail.

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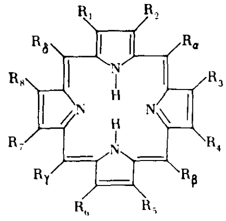
I. INTRODUCTION

Porphyrins belong to one of the most thoroughly investigated classes of organic compounds, owing to their enormous role in biological processes. Several fundamental monographs and reviews devoted to the structure and coordination chemistry of metalloporphyrin[1-5] as well as their reactivity[6] were published in recent years. There are no reviews in the modern chemical literature in which the properties and behaviour of porphyrin molecules in an excited state are discussed. A monograph[2], which is partly devoted to the luminescence of porphyrins, is an exception. However, during the period which has elapsed since its publication, new extensive information has accumulated on the photophysical properties of metalloporphyrins. Furthermore, the photonics of porphyrins is of primary importance for the understanding of the essential features of the processes underlying the initiation of the electron transport chain in photosynthesis and for the control of these processes as well as for the simulation of natural systems suitable for the transformation of light energy into a chemical form. The aim of the present article is to fill the existing gap in the literature and to survey the experimental data on the photonics of porphyrins obtained mainly during the last decade.

Porphyrins are derivatives of porphin–a cyclic system formed by four pyrrole rings linked by methine bridges:



porphyrin
(R = H throughout)

we have etioporphyrin (I; $R_1 = R_3 = R_5 = R_7 = CH_3$, $R_2 = R_4 = R_6 = R_8 = C_2H_5$, $R\alpha = R\beta = R\gamma = R\delta = H$), mesoporphyrin (IX; $R_1 = R_3 = R_5 = R_8 = CH_3$, $R_2 = R_4 = C_2H_5$, $R_6 = R_7 = CH_2CH_2COOH$, $R\alpha = R\beta = R\gamma = R\delta = H$); haematoporphyrin (IX; $R_1 = R_3 = R_5 = R_8 = CH_3$, $R_2 = R_4 = CH_2CH_2OH$, $R_6 = R_7 = CH_2CH_2COOH$, $R\alpha = R\beta = R\gamma = R\delta = H$), octaethylporphin ($R_1 = R_2 = R_3 = R_4 = R_5 = R_6 = R_7 = R_8 = C_2H_5$, $R\alpha = R\beta = R\gamma = R\delta = H$), and tetraphenylporphin ($R_1 = R_2 = R_3 = R_4 = R_5 = R_6 = R_7 = R_8 = H$, $R\alpha = R\beta = R\gamma = R\delta = C_6H_5$). Hydrogenation of the double bond in the pyrrole ring leads to chlorins, the most important representative of which is chlorophyll, while hydrogenation of two double bonds result in the formation of bacteriochlorins, the natural representatives of which transform light energy in bacterial photosynthesis. When methine bridges are replaced by tertiary nitrogen atoms, azaporphyrins are obtained. Structures consisting of four isoindole units linked by methine bridges are called benzoporphyrins. When the methine bridges in tetrabenzoporphin are substituted by nitrogen atoms, tetrabenzo-tetra-azaporphin or phthalocyanine is obtained.

Porphyrins are amphoteric compounds capable of combining two protons via the lone electron pairs of the unsubstituted nitrogen atoms or can exhibit acid properties, giving up two central protons in an alkaline medium. The substitution of the protons by a doubly charged cation results in the formation of chelate complexes—metalloporphyrins. The metal atom in these compounds is linked to the four nitrogen atoms by equivalent chemical bonds. As a result of complex formation, the molecule acquires a fourfold symmetry axis.

II. THE ELECTRONIC STRUCTURE OF METALLOPORPHYRIN MOLECULES

All porphyrins have similar electronic spectra, a characteristic feature of which is the presence in the visible region of four absorption bands and of an intense band, the so called Soret band, at the boundary between the ultraviolet and visible regions. The positions and relative intensities of the absorption bands depend on the nature of the substituents. Fundamental studies have now been carried out on the interpretation of the absorption spectra of porphyrins[2]. It has come to be assumed that the long-wavelength bands in the spectra of both porphyrins themselves and of their metallo-derivatives are due to transitions in the branched π-electron system of the bonds in the tetrapyrrole macroring. This is suggested by the results of quantum-chemical calculations and experimental data. Polarisation measurements[7-9] have shown that the electric dipole moment of the electronic transition lies in the plane of the porphyrin molecule. The weak influence of the solvent on the position of the absorption band is also evidence for the $\pi \rightarrow \pi^*$ type of the lowest excited states. A purely phenomenological approach confirms this conclusion. Indeed the $n \rightarrow \pi^*$ transitions in nitrogen-containing heterocycles occur in the region of approximately 310 nm.[10] If account is taken of the presence of an intramolecular hydrogen bond in the porphyrin molecules, the above absorption should occur at still higher frequencies. The formation of metalloporphyrins is accompanied by significant changes in the spectrum. In the vast majority of cases, the four-band spectrum in the visible region is converted into a two-band spectrum without an appreciable change in the position of the Soret band—the latter merely becomes appreciably narrower.

The positions of the absorption bands of metalloporphyrins depend little on the nature of the central metal atom: the wavelengths of the longest-wavelength maximum varies within the range of 30 nm. A correlation has been observed between the position of this band and the stability of the complex. Thus the stability decreases and λ_{max} increases in the sequence[11-13]

$$\mathrm{Pd} > \mathrm{Pt} > \mathrm{Ni} > \mathrm{Co} > \mathrm{Ag} > \mathrm{Cu} > \mathrm{Zn} > \mathrm{Mg} > \mathrm{Cd} > \mathrm{Ba}\ .$$

It has been noted that, within the limits of the same subgroup in the Periodic System, the stability of the complexes decreases with increase of the atomic number of the central metal atom[11]. The hypsochromic shift of the absorption bands observed as the stability of metalloporphyrins increases, is evidence for the dominant role of σ bonds in complex formation, compared with π-dative bonds, i.e. for a weak interaction of the central metal atom with the π-electron system of the ligand[12]. The electronegativity of the ions increases in the above sequence with increase of the stability of the complexes[14]. A linear relation has been established between the electronegativity of the central ion and the first oxidation potential for a series of metallo-derivatives of porphyrins and chlorins[15,16]. Such correlation is associated primarily with the decrease of the energy of the highest occupied level on enhancement of the electron-accepting properties of the central atom; this should entail also a decrease of the energy of the lowest vacant level. As a result of the latter, smaller reduction potentials of the complex correspond to higher oxidation potentials and conversely. This conclusion is fully consistent with experiment[6].

The similarity of the electronic spectra of the majority of metalloporphyrins and their weak dependence on the nature of the central metal atom are apparently additional confirmation of the fact that the absorption of all the metalloporphyrins is due to the same chromophore. It is noteworthy that the "simplification" of the spectra of porphyrins on formation of metallo-derivatives, noted above, is attributed to the increase of molecular symmetry from D_{2h} to D_{4h}.[17]

The interpretation of the spectra of metalloporphyrins is based on Gouterman's four-orbital model[18,19]†. In this model the optical properties of the metalloporphyrins are accounted for by the electronic transitions from the two highest occupied orbitals to the lowest vacant orbitals taking into account the configuration interaction. The lowest vacant orbitals e_{gx} and e_{gy} of metalloporphyrins are degenerate, while the highest occupied orbitals a_{1u} and a_{2u} are almost degenerate. The $(a_{1u}e_g)$ and $(a_{2u}e_g)$ configurations interact in pairs, giving rise to states in which almost equal dipole moments of the transitions weaken or enhance one another. This leads to the occurrence of a weak Q transition and a very intense B transition corresponding to an absorption band in the visible region and to the Soret band. The longest-wavelength absorption band and the Soret band in the spectra of metalloporphyrins are associated with purely electronic transitions; the second band in the visible region has a vibronic origin[17]. The four-orbital model has been confirmed satisfactorily by the results of numerous spectroscopic studies[2]. The four main transitions in the visible spectra of free porphyrins are interpreted as the daughter transitions Q_x and Q_y and two vibrational transitions. The B_x and B_y transitions are in the region of the Soret band. It is significant that the intensities of the Q_x and Q_y bands are extremely sensitive to substituents, while the intensities of the vibronic bands are almost independent of the nature and positions of the side groups. This factor constitutes a theoretical basis for the classification of porphyrins in terms of spectral types.

The interpretation of the electronic spectra of porphyrins and their metallo-derivatives within the framework of the four-orbital model agrees satisfactorily with the results of studies on magnetic circular dichroism (MCD) and magnetic optical rotatory dispersion (MORD). The magnetic optical activity of tetrapyrrole pigments has been investigated in fair detail[22-36]. Stephens et al.[24] analysed the MORD data[22,23] and confirmed that the visible bands in the spectra of Zn-haematoporphyrin and Mg-phthalocyanine correspond to the vibrational components of the ${}^1A_{1g} \rightarrow {}^1E_u$ transition, while the Soret band corresponds to the second ${}^1A_{1g} \rightarrow {}^1E_u$ transition. It has been found from MCD data that the longest-wavelength bands in the spectra of free porphyrins are due to two electronic transitions, the moments of which are mutually perpendicular and lie in the plane of the molecule. Comparison of the magnetic moments obtained by Stephens et al.[24] with the values calculated by Simpson[27] and Gouterman[19] showed that the four-orbital model leads to data in good agreement with experiment. The interpretation of the absorption spectra of chlorins proposed by Gouterman[19] has also been confirmed by MCD data[24].

Experiment has shown that the set of configurations of the four-orbital model is in many cases quite sufficient for calculations of the spectra of metalloporphyrins. For example the Q state of chlorophyll consists to the extent of 97% of the configurations of the four-orbital model[28]. However, the influence of new configurations introduced into the calculation varies from porphyrin to porphyrin[28], so that in the studies carried out in recent years account is taken of a large number of singly excited configurations. As an example, one may quote the calculation for porphyrin and its zinc complex carried out by the Pariser–Parr–Pople method taking into account all singly excited configurations[29,30]. The electronic structure of the metallo-derivatives is characterised by the occurrence of three low-lying electronic transitions[29]. The first apparently corresponds to the longest-wavelength band and the second and third to the Soret band and its shoulder respectively. Differences from the results obtained on the basis of the four-orbital scheme are observed for porphyrins. According to one calculation[29], three electronic transitions correspond to the Soret band. Bands I and III have been interpreted as purely electronic, and the authors assumed that the third transition in the visible region can refer either to band IV or to the Soret band. The calculated charges on the atoms and the bond orders indicate the presence in the Zn-porphin of two equivalent conjugation chains—inner and outer (Fig. 1*b*). Of the two conjugation chains of free porphin (Fig. 1*a*), that which passes through unsubstituted nitrogen atoms makes the greatest contribution to the charges and bond orders. The conjugation

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† The latter is based on earlier investigations[20,21].

chains served for a long time as models for the early quantum-chemical calculations on porphyrins[31,32].

It has been observed recently that the absorption spectra of metalloporphyrins containing certain ions with powerful electron-accepting properties have an anomalous form. These include derivatives of the dimethyl ester of mesoporphyrin (IX) with $Fe^{III}Cl$, $Bi^{III}OH$, $Mn^{III}Cl$, $As^{III}Cl$, and Hg^{II}, of aetioporphyrin with $Sb^{III}Cl$,[32] and of octaethylporphin with $Mn^{III}OPh$ (OPh is the phenoxy-residue)[34].

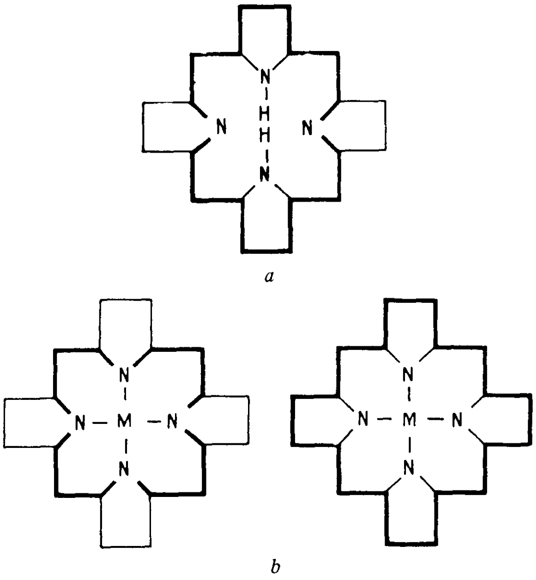

Figure 1. Conjugation chains of porphin (*a*) and metalloporphin (*b*)[29].

In order to be able to understand the nature of the excitation and to elucidate the mechanism of the deactivation of the excitation energy, it is necessary to know the electronic structure of the molecule. For the majority of metalloporphyrins, it has sofar been possible to obtain data for the electronic levels of the central metal atom from quantum-mechanical calculations but not on the basis of spectroscopic studies. Calculations of the energy levels of porphyrins and their metallo-derivatives can nowadays be carried out only by semiempirical methods. The majority of the calculations have been performed by the extended Hückel method (EHM). The series of theoretical studies by Gouterman and coworkers, devoted to the investigation of metalloporphyrins containing Group II–VIII elements (mainly those of the Third Period), are of interest in this sense[35-41].

Fig. 2 illustrates the energy level diagram for metalloporphyrins quoted by Zerner and Gouterman[35]. In the zinc complex the *d* orbitals are located fairly low in the above scheme and are almost completely mixed with the orbitals of the tetrapyrrole ring. The highest occupied orbital is b_{1g}, which is a σ orbital. Cu-porphyrin has a similar electronic structure. In the molecule of this complex the b_{1g} orbital is also below the vacant $e_g(\pi)$ orbital of the porphyrin, but possesses a more distinct $d_{x^2-y^2}$ character than in the zinc derivative. Other *d* orbitals with lower energies resemble the corresponding orbitals of the zinc complex. The b_{1g} orbitals of Ni- and Co-porphyrins are vacant. They lie below the vacant $e_g(\pi)$ orbital or porphin and are almost pure $d_{x^2-y^2}$ orbitals of the metals. The remaining *d* orbitals are occupied and are located between the highest occupied $a_{2u}(\pi)$ levels and the vacant $e_g(\pi)$ levels of the tetrapyrrole ring; the splitting of the *d* levels is approximately 0.05 eV. A distinctive feature of the iron and manganese complexes of porphyrins is the presence of low-lying vacant d_{z^2} and $d(\pi)$ orbitals. The vacant *d* level between the occupied and vacant levels of the tetrapyrrole chromophore creates the necessary conditions for the corresponding intramolecular electronic transitions. Indeed the anomalous absorption spectra of certain iron(III) and manganese(III) complexes of porphyrins, described above, have been attributed to $\pi \rightarrow d(\pi)$ transitions in a number of recent studies[42-44]. We may note that the idea of the interpretation of the absorption bands of Fe-porphyrins as charge-transfer bands was put forward as early as 1957 by Dain and Ashkinazi[45] on the basis of the photochemical behaviour of these compounds.

The quantum-mechanical calculations on metalloporphyrins can be tested by comparison with the results of experiments on the reduction and oxidation of metalloporphyrins. It is then necessary to take into account the fact that, when the pigment molecule is reduced, the electron is localised either at the central ion or occupies a vacant $e_g(\pi)$ orbital of the conjugated bond system. On the other hand, in the oxidation reaction the electron can also be split off either from the central ion or from the organic component of the molecule. The site where the electron is added or abstracted should apparently be determined by the relative positions of the energy levels of the ligand and the metal (within the framework of the simple molecular orbital model).

The available data for the oxidation-reduction reactions of the majority of metalloporphyrins are summarised below:

1. Metal ions which remain stable in the electrochemical oxidation or reduction of metalloporphyrins:
   (a) univalent—alkali metals;
   (b) divalent—alkaline earth metals, Pd, Cu, Zn, and Cd;
   (c) trivalent—Sb, Sc, Al, Ga, In, and Tl;
   (d) tetravalent—Si, Ge, Sn, TiO, and VO.
2. Oxidation-reduction reactions involving the metal atom:
   (a) $M(I) \rightleftharpoons M(II)$—Co;
   (b) $M(II) \rightleftharpoons M(III)$—Mn, Fe, Co, Cr, Ag, and Ni;
   (c) $M(II) \rightleftharpoons M(IV)$—Pb;
   (d) $M(III) \rightleftharpoons M(IV)$—Cr and Fe;
   (e) $M(IV) \rightleftharpoons M(V)$—MoO.

Evidently experiments agree satisfactorily on the whole with calculated data (Fig. 2). The VO, copper, and zinc complexes of porphyrins are exceptions. Indeed, when they undergo electrochemical oxidation, an electron is abstracted from the tetrapyrrole ligand despite the fact that the highest occupied orbital in the molecules of these substances is the $d_{x^2-y^2}$ orbital. In this case explanations based on the EHM calculations for the initial molecules alone are clearly inadequate. The data for the electrochemical reduction have been confirmed by the results obtained in the study of the reduction of metalloporphyrins by electron donors such as alkali metals and anthracene, naphthalene, pyridine, benzophenone, etc. radical-anions[46,47].

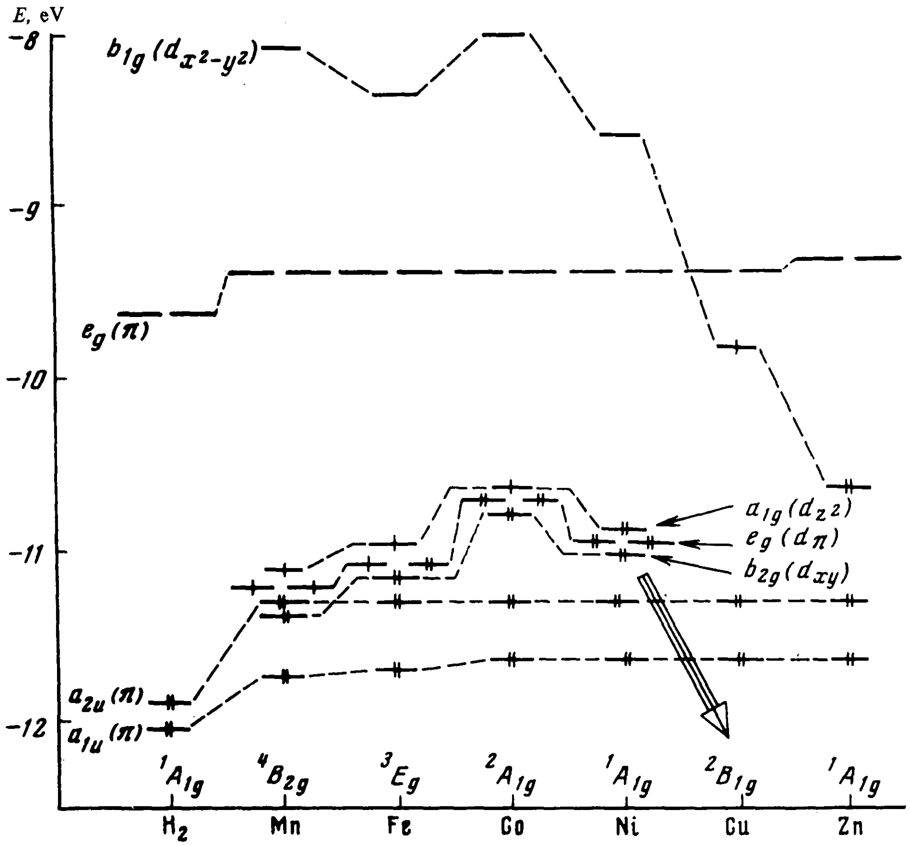

Figure 2. The energy levels of metalloporphyrins[35].

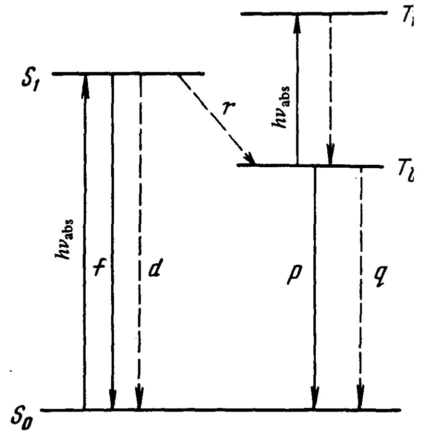

Figure 3. A typical energy level diagram for an organic molecule.

It is of interest that in the case of porphyrins containing transition metal ions oxidation-reduction reactions may lead to compounds with the metal atom in an unusual oxidation state. Thus it is suggested that the electrochemical reduction of Co-sulphophthalocyanine involves the transition of the central metal atom to the zero-valent and univalent states in the primary stages[48]. Evidently in all cases the number of electrons which can add to the central metal atom is determined by the number of vacant levels below the $e_g(\pi)$ electronic level. The compounds formed are of interest from the standpoint of isoelectronic complexes. Such a compound was obtained for the first time by Watt and Davis[49] on reduction of Cu-phthalocyanine by metallic sodium in liquid ammonia. They identified a compound having the composition K_2CuPhc, in which the copper ion has the electronic configuration $3d^{10}4p_1$.

Metalloporphyrins derived from transition metals can combine with up to four electrons in each doubly degenerate $e_g(\pi)$ orbital; the properties of the anions have been thoroughly investigated. Since these data are important for the understanding of the photochemical reduction reactions of metalloporphyrins, they will be considered in detail below.

III. THE LUMINESCENCE SPECTROSCOPIC PROPERTIES OF METALLOPORPHYRINS

The main electronic transitions associated with the step involving light absorption by porphyrin molecules are shown in the simplified diagram in Fig. 3. The probabilities of these processes are determined by the nature of the substituents in the ring and at the central metal atom. We shall consider here only the influence of the metal atom on the photophysical processes in metalloporphyrins.

The Table lists the main luminescence spectroscopic parameters of certain metalloporphyrins. Evidently metalloporphyrins can be divided into three groups in terms of their luminescence properties: (a) complexes of porphyrins with non-transition metals; (b) complexes of porphyrins with the majority of transition metals; (c) complexes of porphyrins with platinum-group metals and also with copper(II) and VO(II).

The luminescence spectroscopic characteristics of metalloporphyrins (φ = quantum yield; τ = phosphorescence and fluorescence lifetime; γ = interconversion quantum yield).

Metal	Porphyrin	φ_{fl}	τ_{fl}, ns	φ_{phosph}	τ_{phosph}, ms	γ	References
Mg(II)	aetio-	0.25	12.0	—	—	0.75	50
	meso-	0.2	—	—	—	0.62	51
Zn(II)	aetop-	0.043	2.8	—	—	0.98	50
	TPP*	0.04	—	—	—	0.92	52
Si(IV)	OEP*	0.20	—	0.018	95	—	53
Ge(IV)	OEP	0.078	—	0.042	42	—	53
Sn(IV)	OEP	0.0078	—	0.068	30	—	53
Pd(II)	aetio-	0.0001		0.5	1.93	—	53, 54
Pt(II)	aetio-	nil	nil	0.9	0.121	—	54
Cu(II)	aetio-	nil	nil	0.6	0.08	—	54
Mn(III)	meso-	nil	nil	nil	nil	nil	53, 54
Fe(III)	meso-	nil	nil	nil	nil	nil	56, 57
Ni(II)	meso-	nil	nil	nil	nil	nil	
Co(II)	meso-	nil	nil	nil	nil	nil	
Ag(II)	meso-	nil	nil	nil	nil	nil	

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*Tetraphenylporphin.

**Octaethylporphin.

(a) Metalloporphyrins containing non-transition metals fluoresce and phosphoresce. It has been shown for various porphyrins that the sum of the fluorescence and intercombination transition quantum yields for these compounds is approximately unity[52,58,59]. Hence it follows that the main pathways to the deactivation of excited porphyrin molecules are fluorescence and transition to a triplet state, while the probability of the radiationless transition from the excited singlet state to the ground state is apparently low. The nature of the axial ligands apparently has virtually no influence on the luminescence properties of porphyrins containing trivalent and tetravalent metal atoms[53,60]. The tabulated data show that, with increase of the atomic number of the central metal atom, the intensity of the fluorescence falls while that of the phosphorescence increases. This finding can be explained by the influence of the heavy inner atom which increases the probability of the intercombination transitions[60]. Indeed, when the central metal atom is replaced by one of a heavier element, all three rate constants r, p, and q for intercombination transitions increase. It is of interest that the central metal atom has the greatest influence on r and the smallest on q. The probability q of intercombination degradation in free porphyrin molecules is greater than in their magnesium and zinc derivatives. This is associated with the involvement of the vibrations of the N–H bonds in the radiationless deactivation of the lowest triplet state of porphyrins[61,62].

(b) Metalloporphyrins containing the transition elements manganese(II), manganese(III), iron(II), iron(III), cobalt(II), cobalt(III), nickel(II), etc. do not fluoresce or phosphoresce. The existence of excited triplet states of these pigments could not be observed either by the usual pulse technique[63] or with the aid of laser photolysis used recently[64,65]. Thus excited states with lifetimes exceeding 10^{-9} s were not observed for these compounds.

(c) Metalloporphyrins containing platinum metals, copper(II), and VO(II) do not fluoresce but phosphoresce intensely. The phosphorescence and intercombination transition quantum yields for many complexes of this group are unity. It is remarkable that the lifetimes of the excited triplet states of the compounds under consideration are much shorter than those of derivatives with non-transition metals. Thus measurements of the lifetimes of the triplets carried out by the laser technique for the copper derivatives yielded $\tau \simeq 9 \times 10^{-4}$ s at 77 K and 1.5×10^{-7} s at room temperature.[65] The presence of the above ions also greatly reduces the lifetime of the excited singlet state. The lifetime of this state has been estimated[66] for the copper and vanadium complexes of porphyrins from the width of the quasi-lines in Shpol'skii's spectra. It proved to be 3×10^{-14} s, while the rate of the intercombination transition was found to be approximately 10^{-13} s^{-1}.

The problem of the mechanism of the deactivation of the excited states of metalloporphyrin molecules containing transition metal atoms is complex. It is simplest to postulate that the influence of the central metal atom tends to increase the rates of the intercombination transitions $S^* \rightarrow T$ and $T \rightarrow S_0$. However, this hypothesis does not show which perturbations cause the very marked increase in the probabilities of the above processes. Presumably the magnetic effects of the ions are insignificant; thus the diamagnetic nickel complexes of porphyrins neither fluoresce nor phosphoresce, while the copper derivatives, containing the paramagnetic copper ion, exhibit an intense phosphorescence. Analysis of the tabulated data shows that the enhancement of the spin–orbital interaction on passing from light to heavier elements also plays a secondary role in the deactivation of the excited states of porphyrin complexes with transition metals. Thus the zinc and cadmium derivatives fluoresce, while metalloporphyrins containing the lighter elements (Fe, Mn, Ni, and Co) do not luminesce at all. The influence of transition metal ions is apparently specific.

As shown in the previous Section, the formation of complexes by porphyrins with metal ions result in the addition of the d levels of the central metal atom to the existing system of the singlet and triplet levels. Depending on the nature of the metal atom, two variants of the relative positions of these two systems of levels are possible (Fig. 4). In the first case (Fig. 4a) the vacant d orbitals are distributed above the vacant $e_g(\pi)$ level of the ligand. Conditions for the transfer of an excited electron to the d levels of the metal do not then exist and the porphyrin is characterised by radiative transitions from the singlet and triplet states. In the second variant (Fig. 4b), the electron may pass from the excited S and T levels to the corresponding vacant levels of the metal. Such transitions should be more probable than the $S(T) \rightarrow S_0$ transitions because of the smaller difference between the energies of the d and π^* states.

The ideas about the specific influence of the central ion on the photonics of metalloporphyrins have been formulated in a general form and developed[45,67] on the basis of the study of the photochemical oxidation and reduction reactions of chlorophyll derivatives containing variable-valence metals. The photochemical activity of complexes containing variable-valence metal ions can be accounted for by the intramolecular electron transfer from the ligand to the central ion. The proposed mechanism of the deactivation of the excited states of metalloporphyrins containing transition metal ions has also received direct experimental confirmation. Thus the effect of a powerful laser pulse on the iron, manganese, and the nickel complexes of porphyrins has been studied[64,65]. The authors were unable to record the absorption for the metastable level of these compounds, but did observe a decrease in the intensity of the absorption band unambiguously related to the "simplification" of the initial state. This finding can be explained in terms of the mechanism of the deactivation of the excited states considered here. In the light of ideas about the interaction of the *d* orbitals of metals with the excited orbitals of the π-electron system, one can explain certain types of "anomalous" behaviour of many metalloporphyrins containing transition metals (Cu, Pd, Pt, and VO).

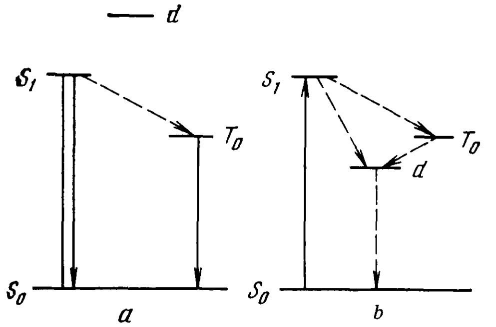

Figure 4. The electronic transitions in metalloporphyrins: *a*) a transition to atomic levels is impossible; *b*) there is no fluorescence and phosphorescence as a consequence of radiationless transitions of excited electrons to low-lying *d* levels.

The nickel complexes of porphyrins do not fluoresce although their vacant orbitals lie below the $e_g(\pi)$ level. This can be explained[68] by the finding that the distance between the d_{z^2} and $d_{x^2-y^2}$ levels is small (Fig. 2) and there is therefore a possibility of the transition of a single paired electron to the $d_{x^2-y^2}$ orbital. Conditions are thereby created for the migration of the excited π electron to the incompletely filled metal orbital.

The situation is different for the luminescence of porphyrins containing platinum-group, copper, and vanadyl ions. In these compounds there are vacant *d* levels located below the excited $\pi\pi^*$ orbitals of the ligand. Furthermore, they are characterised by an intense phosphorescence. The phosphorescence spectra of the copper and VO derivatives of porphyrins consist of two bands[69]. According to Gouterman and coworkers[69,70], the short-wavelength band is associated with the electronic transition from a "triplet-doublet" state, and the less intense band is due to a transition from the quartet state arising as a result of the splitting of the triplet level of the ligand on interaction with the *d* orbitals of the central metal atom. The small energy difference ΔE between the *d* and $\pi\pi^*$ levels constitutes a condition for such interaction. In complexes with much greater ΔE values intramolecular electron transfer is probably responsible for the quenching of the luminescence. The temperature dependence of the luminescence intensity shows that the existence of two phosphorescence bands of Cu-porphyrins is associated with the occurrence of two electronic transitions[69]. When the solution temperature is reduced from 77 to 10 K, the duration of the luminescence increases (by an order of magnitude) and the intensity of the short-wavelength emission band diminishes markedly. This effect of temperature can probably be explained by the fact that the triplet-doublet level is populated partly owing to the thermal activation of the electrons in the doublet level.

The deactivation of the excited states of metalloporphyrins by intramolecular energy transfer to the central metal atom has been observed in the ytterbium complex of tetrabenzoporphyrin[71], in the photochemical excitation of which a weak glow associated with transitions in the metal atom was observed. It is of interest that in this case the electronic excitation energy is degraded already after the step involving energy transfer to the Yb^{3+} ion.

IV. THE PHOTOCHEMISTRY OF METALLOPORPHYRINS

According to modern ideas, chlorophyll undergoes oxidation-reduction reactions following the initiation of the electron transport chain during photosynthesis. The electron phototransport reactions are therefore of greatest interest for investigation. The photochemical properties of natural porphyrins—chlorophyll and bacteriochlorophyll—have of course been investigated most thoroughly. In 1948 Krasnovskii discovered the phenomenon of the reversible photochemical reduction of chlorophyll[72], which initiated the extensive and systematic study of the photonics of tetrapyrrole pigments.

It follows from the analysis described in the previous section that the electronic structure of the central metal atom determines the photophysical properties of porphyrin compounds. In consequence of this, the metal atom must influence also the reactivity of the excited molecule.

Electron phototransport with participation of porphyrins apparently has the same features as those of the photochemical reactions of other classes of organic compounds. According to a generally accepted view, any oxidation-reduction reaction in solution includes three stages: the formation of complexes, electron transfer within the reaction complex, and decomposition of the latter. Intermediate complexes may be formed from molecules either in the ground state or in an excited state:

$$P + A \rightarrow P^{+}A^{-} \xrightarrow{h\nu} [P^{+}A^{-}]^{*} \longrightarrow \left| \begin{array}{l} \longrightarrow P + A \\ \longrightarrow P^{\dot{+}} + A^{\dot{-}} \end{array} \right. , \qquad (1)$$

$$P \xrightarrow{h\nu} P^{*} \quad P^{*} + A \rightarrow [P^{+}A^{-}]^{*} \longrightarrow \left| \begin{array}{l} \longrightarrow P + A \\ \longrightarrow P^{\dot{+}} + A^{\dot{-}} \end{array} \right. , \qquad (2)$$

where P is the porphyrin and A the electron acceptor.

The occurrence of the reaction via the first or second pathway is determined by the oxidation-reduction properties of the reacting molecules and the characteristics of their excited states. For the reaction to proceed via mechanism (**2**), the following condition must be fulfilled:

$$\frac{1}{\tau_0} \ll k_{\text{diff}}\,[A],$$

where τ_0 is the lifetime of the excited state, k_{diff} the rate constant for the diffusion of molecules (in non-viscous liquids at room temperature, $k_{\text{diff}} \simeq 10^{10}$ litre mole^{-1} s^{-1}), and [A] is the concentration of the reactant. Metalloporphyrins containing transition metals do not satisfy the condition formulated above ($\tau_0 \ll 10^{-9}$ s). Electron phototransport in such cases apparently takes place only when the complexes formed under dark conditions are acted upon by light. Thus Fe(III)-phaeophorbide is reduced only when the introduction of an electron donor into the solution causes a change in the absorption spectrum of the initial pigment, indicating the formation of a complex[73].

The introduction of electron donors and acceptors into solutions of fluorescent metalloporphyrins is accompanied by a decrease of the fluorescence quantum yield. In general the quenching of the fluorescence is a complex phenomenon and can be due to various factors. Dilung and Chernyuk[75,76] concluded on the basis of the correlation between the degree of quenching of the fluorescence of pigments of the chlorophyll series and the redox potentials of the fluorophore and the quenching agents (aromatic nitro-compounds and hydrazine derivatives) that the quenching of the fluorescence is based on electron transfer. Subsequently this was confirmed in the quenching of the fluorescence of Mg-phthalocyanine and ethylchlorophyllide[77,78], tetraphenylporphin and its zinc derivative[79], and pyrochlorophyll[80] by nitro-compounds and of the fluorescence of chlorophyll by quinones[81,82]. The study of the quenching of the fluorescence can provide an answer to the question whether electrons are transferred via mechanism (1) or (2). It was stated above that the choice between these mechanisms is determined primarily by the donor–acceptor properties of the interacting molecules. One should therefore probably only consider whether or not a particular type of interaction predominates.

The study of the quenching of the fluorescence of Zn-phthalocyanine by aromatic amines has shown that the degree of quenching is greater than might have been expected from the complex-formation constant in the ground state[83]. This is probably evidence for the simultaneous occurrence of the competing processes (1) and (2), which are responsible for the quenching. Similarly it has been concluded[84] that the quenching of the fluorescence of mesoporphyrin (IX) by *m*-dinitrobenzene is due to the complex formation reaction between them, both in the ground and excited states, but the role of the latter is significantly greater. The study of the dependence of the lifetime of the excited singlet states of porphyrin molecules on the concentration of *m*-dinitrobenzene[85] and the dependence of the constants for the quenching of the fluorescence of chlorophyll and its analogues by benzoquinone on solvent viscosity[86] also provided grounds for the conclusion that there is competition between the two types of quenching; it has been shown that the dynamic mechanism (2) makes the main contribution. It is interesting that, even in the case of a powerful acceptor such as 1,3,5-trinitrobenzene, the quenching effect is not wholly due to the formation of a charge-transfer complex in the ground state[85].

On interaction with electron acceptors, porphyrin molecules exhibit powerful π-donor properties. This is indicated primarily by the high formation constants of the charge-transfer complexes[88]. The charge-transfer bands of complexes with powerful electron acceptors such as 7,7,8,8-tetracyanoquinodimethane, 1,2,4,5-tetracyanobenzene, and tetracyanoethylene (TCE) are in the infrared and are observed only at low temperatures[89]. It is of interest that the position of the charge-transfer band depends only slightly on the nature of the central metal atom. This is apparently a consequence of its weak interaction with the π-electron system of the ligand. On the other hand, the powerful influence of the lateral substituents of the tetrapyrrole ligand on complex formation is incomprehensible. It follows from the available data[89] that the absorption band arising when Zn-aetioporphyrin reacts with TCE is located at 1070 nm, while that due to the reaction of Zn-tetraphenylporphin with the same acceptor is at 900 nm.

There are data showing that in the case of metalloporphyrins containing transition metal atoms electrons may be transferred from the *d* levels of the metal. Thus a study has been made[90] of the interaction of Co-tetraphenylporphin with tetracyanoethylene and it has been shown that the system contains complexes of two types: $[\text{Co(II)TPP}]^{+}.[\text{TCE}]^{-}$ and $[\text{Co}^{+}\text{(III)TPP}].[\text{TCE}]^{-}$. When the second complex is formed, an electron is transferred from the *d* orbital of the cobalt atom to TCE.

The electron transfer schemes show that the primary products arise in a single solvent "cage". This creates favourable conditions for their recombination. There is no doubt that the usually observed low quantum yields of photochemical processes are associated with this factor[91]. However, when there is a possibility of reactions which eliminate one of the radical-ions from the system, the photochemical oxidation quantum yield increases. An elegant procedure was used by Bobrovskii and Kholmogorov[92]. In the oxidation of chlorophyll and Zn-aetioporphyrin they used tetranitromethane as the electron acceptor, which decomposes, following the addition of an electron, into NO_2 and $\bar{C}(NO_2)_3$.

The properties of excited complexes formed by porphyrin molecules with electron acceptors and donors are of undoubted interest. The hypothesis of the existence of chlorophyll exciplexes was put forward for the first time by Dain and Dilung[93] in connection with the analysis of the results of the quenching of the pigment fluorescence by aromatic nitro-compounds. The formation of exciplexes was postulated as an intermediate stage in the photochemical oxidation of chlorophyll. However, this was not confirmed by experimental data.

In the presence of electron acceptors the intensity of the fluorescence spectra of tetrapyrrole pigments as a rule decreases in parallel with increase of the concentration of the acceptor without the appearance of new emission bands[94]. On the other hand, the interaction of chlorophyll with electron donors (amines and pyridine derivatives) leads to a shift of the fluorescence band without an appreciable change in the absorption spectrum[95]. The authors attribute this finding to the interaction of the excited chlorophyll molecules with electron donors, leading to the formation of fluorescent exciplexes.

Data[66] for the formation of ternary exciplexes, including, apart from chlorophyll, electron donors (amines, pyridine bases, and esters) and acceptors (nitro-compounds) merit attention. The conclusion that ternary exciplexes are formed was reached on the basis of changes in the fluorescence spectra of the pigment in the presence of the above compounds. Later similar ternary exciplexes were observed for tetraphenylporphin and its zinc derivative[79]. It is significant that the formation of ternary exciplexes facilitates electron phototransfer from the porphyrin compound to the acceptor. This is confirmed by the fact that the formation of exciplexes is accompanied by a significant increase of the fluorescence quenching constants[96] and by an increase of the photopotentials and photoconductivity[97]. The authors regard the ternary exciplexes as analogues of D → M → A complexes, which, according to Shilov's ideas[98], play the role of a transition state in dark heterolytic reactions.

The ESR spectra of both radical-cations and radical-anions of the majority of tetrapyrrole pigments consist of narrow lines without any signs of a hyperfine structure[99-101]. This indicates a high degree of delocalisation of the charge in the π-electron system of the tetrapyrrole ligand. Indeed, with increase of the extent of the π-electron system on passing from porphyrins to phthalocyanines, the ESR spectra of both radical-cations and radical-anions become narrower still[100]. The radical-anion forms of tetrapyrrole pigments are highly reactive. The radical-cations are powerful oxidants, while the radical-anions exhibit a considerable tendency towards protonation reactions. Their short lifetime in solution is due to this factor.[102]

The high reactivity of the radical-ion forms of pyrrole macrorings is responsible for their involvement in sensitisation processes. Krasnovskii[104,105] and Evstigneev[103] investigated the interaction of the primary photochemically reduced forms of chlorophyll and other photosensitising pigments with electron acceptors (Methyl Red, Acid Orange, Safranine T, riboflavin, etc.). The mechanism of the involvement of the radical-anions of tetrapyrrole heterocycles in photosensitised oxidation-reduction processes was proved by these investigations. Direct evidence for the involvement of the primary oxidised form of chlorophyll in the sensitisation of oxidation-reduction reactions has been published[106]. In a study of the sensitising action of chlorophyll and phaeophytin on the photochemical oxidation of the leuco-bases of triphenylmethane dyes (Malachite Green and parafuchsin) by nitro-compounds a correlation was found between the yield of the process and the oxidation potentials of the nitro-compounds. On this basis, it was concluded that the primary sensitisation reaction involves the photochemical oxidation of the pigment.

It was mentioned earlier that, depending on the relative positions of the vacant energy levels of the metal atom and the ligand, either the tetrapyrrole ligand or the central metal atom is reduced. This was also shown for the photochemical reduction of metalloporphyrins containing titanium-subgroup[107] and also manganese(III), iron(III), and cobalt(III) ions[108]. The elimination of an electron from the tetrapyrrole ligand or its addition to the latter leads to profound spectroscopic changes associated with the alteration of the chromophoric system of the molecule. Changes in the valence state of the central metal atom as a rule entail merely a displacement of the absorption bands and a redistribution of their intensities.

Irradiation of Mn(III)-, Fe(III)-, and Co(III)-porphyrins in the presence of reductants leads to the reduction of the central metal atom[108].

Iron(III) and manganese(III) derivatives of phaeophytin and phaeophorbide are of considerable interest from the standpoint of models of the second photosynthetic system. It has been shown[109,110] that these compounds are reduced by hydroxide ions on irradiation with visible light. In order to interpret these results, the concept of the so called intramolecular sensitisation of the photochemical oxidation and reduction processes was put forward[45]. According to this hypothesis, when the π-electron system of the porphyrin skeleton is excited, an electron is transferred to the vacant *d* orbital of the metal. The charge deficiency is made good by an electron of the electron donor present in the system.

It is of interest that metalloporphyrins are photochemically inactive in relation to divalent transition metals. Thus irradiation of copper(II), manganese(II), cobalt(II), and iron(II) complexes in the presence of reducing agents does not lead to changes in the absorption spectra. Furthermore, these complexes are readily hydrogenated by hydrogen at the instant of their isolation[111]. Their photochemical stability is probably associated with the short lifetime of the excited states.

The complexes of porphyrins containing central atoms of non-transition elements readily undergo photochemical reduction.

The photochemical reduction of porphyrin molecules is a multistage reaction including several dark and photochemical stages. It was already shown in the early studies that the primary reaction products are radical-anions[112]. Investigation of the interaction of porphyrin molecules with electron donors showed that porphyrins combine with an electron whilst in the triplet state[113].

As mentioned above, the radical-anions of tetrapyrrole systems exhibit a high proton affinity. A mechanism for their protonation reactions has been put forward[114]. The first stable product of the protonation reaction of metalloporphyrins is a substance with an intense absorption band in the range 435–465 nm. On the basis of NMR spectra, the structure of dipyrromethene (PH_2) was attributed to it[115]. It was suggested that it is formed as a result of the disproportionation of the monohydro-derivative ($PH^{\cdot}$) arising in the first hydrogenation stage:

$$P^{-} + H^{+} \rightarrow PH^{\cdot},$$
$$2PH^{\cdot} \rightarrow PH_2 + P^{-\cdot}.$$

Next, PH_2 may interact with the bases[114,116]:

$$PH_2 + OH^{-} \rightarrow PH^{-} + H_2O\ .$$

The PH^- spectrum is characterised by absorption bands in the range 435–465 and in the region of 800 nm.[114] On interaction with atmospheric oxygen, PH^- and PH_2 regenerate the initial metalloporphyrin.

The products of the protonation of the radical-anions of metalloporphyrins described above (PH^- and PH_2) are obtained in the majority of cases together with chlorins and bacteriochlorins on photochemical reduction of metalloporphyrins in solution.

There is no unanimous view in the literature concerning the relation between these porphyrin hydrogenation products. The majority of workers believe that chlorins are obtained from the products PH^- and PH_2 as a result of dark isomerisation[117-120]. On the other hand, others[121] postulate the formation of chlorins independently of the formation of PH^- and PH_2. It has been suggested[119] that the isomerisation is a photochemical reaction.

The isomerisation of the "reversible product" of the reduction of PH_2 to chlorin[119] under the influence of an acid was demonstrated recently. The stronger the acid, the higher the rate of reaction[122]. The study of the transformations of chlorin and PH^- revealed that, on keeping a solution of Zn-chlorin in t-butyl alcohol for 37 h at 130°C in the presence of KOH, the chlorin is completely converted into the "reversible product".[123]

In this connection the results of a study of the photochemical reduction by hydrazine-hydrate of porphyrin compounds containing atoms of aluminium-subgroup elements are of special interest[124]: by employing light at different wavelengths, it was shown that the conversion of the primary hydrogenated species into a product of the chlorin type takes place in the course of a multiphoton reaction. Under the influence of light corresponding to the long-wavelength maximum of the metalloporphyrin (TPP.InBr) at 600 nm, a product is formed with absorption bands at 450 and 800 nm, i.e. apparently PH^-. It is converted into chlorin under the simultaneous influence of light with $\lambda > 700$ nm and 510 nm. The rate of formation of chlorin from PH^- under these conditions is proportional to the intensity of the light raised to the power 1.5. Thus, apart from the photochemical stages in the formation of primary hydrogenated forms (PH^- and PH_2), further transformations of the "reversible products" are also photochemical:

$$P \xrightarrow{h\nu_1} PH^- \underset{\text{dark}}{\overset{h\nu_2}{\rightleftarrows}} z \xrightarrow{h\nu_3} \text{Chl.}$$

The multiphoton mechanism of the photochemical reduction of porphyrins was also demonstrated for the remaining pigments containing aluminium-subgroup elements as well as zirconium and hafnium[107].

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Electron Diffraction Studies on Stereochemically Non-rigid Molecules

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Electron diffraction data for the structures and potential energy functions of molecules with a certain type of intramolecular motion—high-amplitude motion—are analysed in detail and the fundamental characteristics of such motion and the conditions for its experimental observation are formulated. Important structural-chemical consequences of high-amplitude motion and the urgent need for a comprehensive investigation of stereochemically non-rigid molecules are demonstrated.
The bibliography includes 201 references.

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I. INTRODUCTION

Owing to the comparative simplicity of the experimental technique and methods and the possibility of investigating complex molecules (including non-polar molecules), modern gas-phase electron diffraction is of primary importance for the analysis of molecular structures. The main information which can be derived by electron diffraction concerns the geometrical parameters characterising the steric structure as well as the mean square amplitudes of the vibrations of pairs of nuclei. The application of this method in the study of organic and inorganic molecules led to the accumulation of extensive experimental data on molecular structures in the gas phase (see, for example, the compilation in Ref. 1 as well as the relevant reviews[2-10]).

A special type of intramolecular motion of nuclei—the so called high-amplitude motion—has been detected by electron diffraction only in a comparatively small number of molecules; however, it is difficult to overestimate the importance of detailed investigation of this phenomenon for many branches of modern chemistry.

The high-amplitude motion of nuclei is characterised by low frequencies (usually below 100 cm^{-1}) and is reflected specifically in the structure, dipole moments, and other molecular properties. This is manifested in the study of spectra, thermodynamic properties, the behaviour of molecules in electric fields, and other experimental research. Investigations in recent years have provided many examples of the manifestation of complex intramolecular motions of nuclei in compounds of different classes. In this connection, the problem has been assuming increasing current chemical importance in the interpretation of data derived by a wide variety of experimental methods, in the theoretical study of the geometrical and electronic structures of polyatomic molecules, in the calculations of thermodynamic functions of substances, etc.

This review deals with a limited topic—the electron diffraction study of molecules with a complex motion of nuclei (high-amplitude vibrations)†; studies of internal rotation have been excluded, to some extent arbitrarily, because there already exists an independent and exhaustive literature on this problem (see, for example, the review of Bastiansen et al.[15] and the monograph of Orville-Thomas[16]).

II. THE GENERAL CHARACTERISTICS OF THE HIGH-AMPLITUDE MOTION AND THE CONDITIONS FOR ITS EXPERIMENTAL OBSERVATION

It is difficult to define rigorously the concept of "high-amplitude motion" because the nuclear shifts in molecules do not vary continuously. The convention has been adopted that one speaks of the high-amplitude motion of nuclei in those cases where the nuclear shifts are much larger than in the usual motion in "quasi-rigid" molecules, where the nuclei execute small oscillations about the corresponding equilibrium positions[17-19]. Large nuclear shifts arise when periodic internal rearrangements of individual atoms or whole molecular fragments take place in the molecule. The transition of the system of nuclei from one steric configuration to another—the so called hindered motion—constitutes in fact high-amplitude

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† Among the experimental methods for the investigation of processes involving intramolecular motion, NMR also plays an important role. In particular, extensive information has been obtained by this method about the high-amplitude motion of nuclei in the condensed phase (see the relevant reviews[11-14]).

motion and the molecules where such transitions occur are referred to as stereochemically non-rigid‡.

In principle any molecules with identical nuclei can have several steric configurations differing from one another as a result of nuclear transpositions, provided that these transpositions are not equivalent to the rotation of the molecules as a whole. In addition, each non-planar molecules can have left- and right-hand configurations whose interconversion requires inversion. Thus the motion of nuclei in the majority of molecules is generally speaking characterised by potential functions (in the general case potential surfaces) with two (or more) minima corresponding to different steric configurations of the nuclei and separated by potential barriers.

We shall now consider the conditions under which high-amplitude motion is possible in principle and can be observed experimentally.

(a) If the potential function minima are fairly deep (i.e. the barriers between the minima are high), one may assume that a definite steric configuration of the nuclei corresponds to each potential energy minimum.

A quantitative criterion of the fundamental distinguishability of a particular configuration of the nuclear system is (Bersuker[30], p.192):

$$\tau \gg T\ , \qquad (1)$$

$$\Delta E \gg 2\hbar\omega, \qquad (1a)$$

where τ is the "lifetime" of the configuration corresponding to the potential minimum, T the period of the vibrations at the minimum, ΔE the depth of the minimum, and ω the vibration frequency at the minimum. When condition (1) or (1a) is fulfilled, the configuration of the nuclei corresponding to the given minimum is fairly long-lived, quasi-stationary, and in principle can be distinguished experimentally. For an approximate description of the nuclei in the configuration corresponding to the potential energy minimum, the thoroughly developed model of quasi-rigid molecules is applicable[17-19].

In the case under consideration the equilibrium configuration corresponding to the potential minimum is a characteristic of the steric arrangement of the nuclei. The transitions of the system fron one minimum to another can occur as a result of tunnelling through the potential barrier, but such transitions are not always observed experimentally.

If the thermal energy of the molecules kT is greater than the height of the potential barrier, there is an appreciable increase of the population of the upper (above the barrier) vibrational levels. In order to characterise the geometrical configuration of the molecule in these states, it is necessary to know values averaged with respect to the vibrations, which differ appreciably from the equilibrium values corresponding to the potential minima. A typical example of such a case is provided by the ammonia molecule for which there exists two equilibrium nuclear configurations arising when the nitrogen atom is reflected in the plane containing the hydrogen atoms. The vibrational and rotational spectra of the molecules as well as electron diffraction data can be interpreted satisfactorily on the hypothesis of a quasi-rigid pyramidal molecular model, while tunnelling is revealed by the inversion-induced splitting of the vibrational levels in the spectra.

If all the potential barriers separating energetically equivalent configurations are very high (virtually impossible to overcome), one can ignore the existence of all the potential minima except one. The molecular state at this minimum will be stationary and the transitions of systems from one minimum to another will hardly occur.

(b) If the minima in the potential function are shallow (the barriers between the minima are low), i.e. Eqn.(1a) does not hold, then the nuclear system does not possess a definite symmetry and is not characterised by a stable stationary configuration corresponding to the potential minimum. The equilibrium configuration loses the significance of a characteristic of the steric arrangement of the nuclei. In this case individual configurations corresponding to various minima of this type are in principle indistinguishable and the system merely executes periodic virtually unhindered transitions from one configuration to another (or others), i.e. high-amplitude motion arises. As an illustration, one may quote the cyclopentane molecule. In this molecule the motion of the ring nuclei during vibrations can be described as continuous transitions between ten configurations with C_2 symmetry and ten configurations with C_s symmetry ("pseudorotation" of the ring; see Section V below), none of which is a stable equilibrium configuration of the ring.

It is seen from the above examples that in reality one encounters most frequently cases where the total potential energy function possesses at the same time very high barriers, separating the minima from one another, the transitions between which cannot be neglected, and one (or a few) relatively low barriers. For this reason, as a rule only part of the molecule is stereochemically non-rigid in the above sense and the nuclear system executes high-amplitude motion only along one or several but not all vibrational coordinates. Thorson and Nakagawa[31] introduced the concept of quasi-symmetry for molecules with high-amplitude nuclear motion. For example, molecules characterised by a continuous reversible transition from a bent to a linear configuration and conversely are regarded as quasi-linear (quasi-linearity relative to the deformation angle; the molecule is quasi-rigid relative to the other vibrational coordinates).

We shall analyse in greater detail the conditions under which high-amplitude motion may be observed experimentally. Evidently the characteristic time of the experimental method employed should play an important role in this. Indeed, individual nuclear configurations, corresponding to the potential minimum, will be experimentally indistinguishable when the characteristic time τ' of the given experimental method (the time of the effective interaction between the molecular system investigated and the external perturbation) is greater than the lifetime τ of the individual configurations (see Bersuker[30], p.190), i.e.

$$\tau' > \tau, \qquad (2)$$

In this case there is sufficient time during the measurement for the system to undergo repeated transitions from one set of configurations to another, and an average pattern is recorded experimentally. It is easily seen that the fulfilment of condition (2) is facilitated by low values of τ, i.e. low energy barriers between individual configurations.

On the other hand, when

$$\tau' < \tau, \qquad (3)$$

---

‡ The term "stereochemically non-rigid molecules" was introduced by Muetterties[20-27]. In the NMR system other terms are also widely used in the description of the high-amplitude intramolecular motion, for example, "fluctuating molecules"[11], "degenerate intramolecular rearrangement"[13,28], "autoisomerisation"[29], etc.

then a separate configuration is manifested in the measurement with a lifetime τ (provided that it is distinguishable in principle; see above). The times τ' are different for different experimental methods (see Table) and the results of the measurements therefore depend primarily on the method employed [the rule governing the relation with the means of observation (see Bersuker[30], p. 191)].

The characteristic times τ' of certain physicochemical methods[20]*.

Method	τ', s
Electron diffraction	10^{-18}
Neutron diffraction	10^{-18}
X-Ray diffraction	10^{-18}
Ultraviolet spectroscopy	10^{-15}
Visible spectroscopy	10^{-14}
Infrared and Raman spectroscopy	10^{-13}
ESR	$10^{-4}-10^{-8}$
NMR	$10^{-1}-10^{-9}$
NQR	$10^{-1}-10^{-8}$
Mössbauer spectroscopy	10^{-7}
Deflection of molecular beams in electric field	10^{-6}

*The characteristic time of the electron diffraction experiment quoted was obtained by the authors of the review and differs from the value (10^{-20} s) in the literature[13,20].

On the other hand, since the lifetime depends on the vibrational state v at the minimum potential ($\tau = \tau_V$), the fulfilment of conditions (2) and (3) is also determined by the conditions of the measurements, for example, temperature [the rule governing the relation with the conditions of measurement; (see Bersuker[30], p. 190]. Thus the values of τ_V are high at low temperatures and condition (3) may hold for the given τ', i.e. a separate configuration with a lifetime τ_V is observed experimentally. At higher temperatures, higher vibrational levels begin to be populated and τ_V diminishes, which promotes the transition to condition (2) and an average pattern reflecting the high-amplitude motion is manifested experimentally.

The knowledge of the potential function describing the motion of the nuclei in the molecule can yield the complete characteristics of the behaviour of the nuclei, including their high-amplitude motion. However, a rigorous quantum-mechanical solution of the problem of the derivation of such a potential function in the general case is impossible because of the difficulties in the solution of the Schrödinger equation for the electronic states of complex molecules, which cannot as yet be overcome. Additional difficulties in the solution of this problem can be due to the possible deviations from the adiabatic approximation, since there is reason to believe that the vibronic interaction, which has a particularly marked effect when the electronic states are degenerate (the Renner and Jahn–Teller effects) or pseudodegenerate (the Jahn–Teller pseudoeffect), plays a major role in complex intramolecular motion of nuclei. These problems have been examined in detail by Renner[32], Jahn and Teller[33], van Vleck[34], Öpik and Pryce[35], Liehr[36], Longuet-Higgins[37,38], Bersuker[30,39–43], and many other workers (for further details, see the relevant monographs[30,44,45] and reviews[38,43]). Despite these difficulties, useful information about the potential energy functions may be obtained by LCAO-MO calculations[30,46].

The most promising approach to a quantitative description of the motion of nuclei in the case under consideration consists at present in separating the high-amplitude motion from other types of nuclear motion, specifying a definite type of potential function, and solving the corresponding Schrödinger equation for the vibrational and rotational states of the molecule. However, even this more specific problem is complicated, since the thoroughly developed procedure for calculations in terms of normal coordinates and the standard expansion of the potential energy function in terms of these coordinates is of only limited applicability in this instance. A promising approach involves the use of more general curvilinear coordinates with a corresponding increase in the complexity of the expression for the kinetic energy operator and generalisation of the concept of reduced mass. However, these methods have so far been used only in the study of three-, four-, and five-atomic molecules and molecules with pseudorotation in the rings (see, for example, Refs. 47–53). Still more complicated cases, where it is impossible to separate high-amplitude motion from other types of nuclear motion, have not so far been considered.

The application of electron diffraction to the study of stereochemically non-rigid molecules yielded in all cases a qualitative pattern of nuclear motion and sometimes also complete quantitative information about the parameters of the potential functions of such motion. Quantitative data have in fact been obtained only in relatively simple cases where the potential function depends on only one vibrational coordinate (the one-dimensional vibrational problem). In this case there is a complete analogy with internal rotation. This made it possible to employ in the structural analysis of stereochemically non-rigid molecules the classical form of the probability density function, proposed previously[54,55] in relation to internal rotation. The parameters of the potential energy function are determined in most cases by the method of least squares. Either calculated and experimental scattering intensities (radial distribution functions)[56–58], or calculated and experimental vibration amplitudes, or the internuclear distance contraction effects[59] were then compared.

Since the contribution to the intensity of the scattering of electrons by pairs of nuclei executing high-amplitude motion decays rapidly with increase in the scattering angle, it is sometimes useful and effective to analyse low-angle scattering[60–62].

III. QUASI-LINEAR MOLECULES

The motion of nuclei in quasi-linear molecules is one of the simplest cases of high-amplitude motion, because the only vibrational coordinate describing this motion is the change in the deformation angle α. The dependence of potential energy of the quasi-linear molecule on α is illustrated in Fig. 1. One must note that α varies in the region of positive values ($0 < \alpha < \pi/2$), because the configurations corresponding to the potential minima illustrated in Fig. 1 can be derived from one another by the appropriate rotation of the molecule as a whole. The vibrational potential therefore has actually only one minimum, two minima arising on the curve in Fig. 1 when one considers the section of the potential surface taking into account both the deformation vibration and the rotation of the molecule as a whole. This type of situation holds for any planar molecules (see Herzberg[17], pp. 39, 239).

The carbon suboxide molecule C_3O_2 [O(1) = C(2) = C(3) = C(4) = O(5)] is the most thoroughly investigated of the quasi-linear molecules. In the first modern electron diffraction study on the C_3O_2 molecule §[63] unusually high values of the so called "contraction effect" (see Cyvin[64], Chapter XIV) and the vibration amplitudes of pairs of nuclei, the distances between which vary during the deformation vibration, were already observed. The measured quantities did not agree with the theoretical calculations in terms of the approximation of low-amplitude harmonic vibrations[65]. In their experiments at different temperatures (237, 290, and 508 K) the authors[63] attempted to determine the temperatures of the C_3O_2 vapour flowing from the nozzle on the basis of the measured vibration amplitudes and contraction effects. Despite the failure of this attempt, the conclusion that the ν_7 deformation vibration of the C=C=C fragment is not described by a harmonic function must be regarded as an important result of this study[63]. The equation proposed[63] for the potential is (Fig. 1)

$$V(q) = Aq^4 + Bq^2, \tag{4}$$

where A and B are constants and q represents half the deviation of the C=C=C angle for the linear value:

$$q = \frac{180° - \angle\,(\mathrm{C{=}C{=}C})}{2}.$$

According to the authors' estimate, the barrier for the linear configuration is in the range 40–255 $\mathrm{cm^{-1}}$.

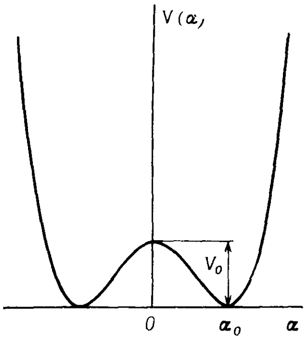

Figure 1. The potential function for the deformation vibration of quasi-linear molecules.

The C_3O_2 molecule was thoroughly reinvestigated by electron diffraction in another study[59], attention being concentrated on the potential function of the deformation vibration of the C=C=C fragment. Using this function, as defined by Eqn. (4), Tanimoto et al.[59] obtained the following expression by analysing the experimental data

$$V(Q_7) = (24 \pm 5)\,Q_7^4 - (100 \pm 31)\,Q_7^2, \tag{5}$$

where $Q_7 = (\sin\alpha)/0.145$ is the vibrational coordinate of the deformation of the C=C=C fragment (α has the same significance as q in the previous notation). The positions of the potential minima correspond to $\alpha_0 = \pm 12°$ and the height of the potential barrier at $\alpha = 0$ is $100 \pm 47\ \mathrm{cm^{-1}}$, the electron diffraction data proving virtually insensitive to the presence or absence of this barrier.

Using Eqn. (5) for the potential of the deformation vibration of the C=C=C fragment and the harmonic approximation for other types of vibration, the authors[59] obtained a satisfactory agreement between the calculated and experimental mean square vibration amplitudes and contraction effects. The vibrational-rotational ν_7 band was also calculated by Eqn. (5) and its maximum proved to be at 70 $\mathrm{cm^{-1}}$, which differs slightly from the experimental value $63 \pm 2\ \mathrm{cm^{-1}}$.[66,67]

The deformation vibration of the C=C=C fragment has been examined theoretically[68] on the basis of spectroscopic and electron diffraction data. Using the method of Thorson and Nakagawa[31], Clark and Seip[68] established by solving the Schrödinger equation for the vibrational and rotational states of the molecule that a potential function of the type

$$V(r) = 2400r^2 + \frac{14000}{2.2 + r^2}, \tag{6}$$

where $r = \alpha r[\mathrm{C(3){=}O(5)}]$ with minima at $\alpha_0 = \pm 10.8°$ and a barrier 50.6 $\mathrm{cm^{-1}}$ high at $\alpha = 0$, describes satisfactorily both spectroscopic and electron diffraction data. Calculation of the position of the absorption band maximum corresponding to the ν_7 vibration by Eqn. (6) yields a value in the range 65–69 $\mathrm{cm^{-1}}$, in good agreement with the experimental value $\nu_7 = 63 \pm 2\ \mathrm{cm^{-1}}$.[66,67] The parameters of the calculated peak of the radial distribution curve, corresponding to the distance between the oxygen atoms, agree just as well with the results of the electron diffraction experiment at 237 and 508 K.

It has also been concluded[68] that electron diffraction data are not unduly sensitive to the detailed form of the potential describing the ν_7 vibration. The potential function (6) and equations of the type

$$\left.\begin{aligned} &V(r) = \text{const}, \ \text{when} \ |\alpha| < 10.8° \ \text{and} \\ &V(r) = 2400r^2 + \frac{14000}{2.2 + r^2}, \ \text{when} \ |\alpha| \geqslant 10.8° \end{aligned}\right\} \tag{7}$$

describe with almost equal accuracy the experimental peak of the radial distribution curve corresponding to the distance between the oxygen atoms.

Another important result obtained in the above investigation[68] was that the use of the classical probability density function

$$P(\alpha) = N e^{-\frac{V(\alpha)}{kT}}$$

leads to virtually the same parameters of the peak on the radial distribution curve corresponding to the distance between oxygen atoms as the quantum-mechanical expression based on the use of 93 vibrational-rotational wave functions in combination with the Boltzmann distribution.

Numerous spectroscopic studies on the carbon suboxide molecule[66,67,69–74] demonstrated a complex structure of the absorption spectra. The absorption bands were assigned and the fine structure and the complex shape of the bands as well as the presence of numerous "hot" bands were explained by experimenters on the basis of potentials of types (4)–(6) for the ν_7 vibration. The problem of the C_3O_2 molecular structure therefore appeared to be solved in broad outline.

[§] We shall not consider the earlier electron diffraction studies (see, for example, the compilation in Ref. 1).

However, a high-resolution infrared spectrum (0.3 cm^{-1}) was obtained in 1973 in the range 20–80 cm^{-1} as well as the Raman spectra of the C_3O_2 molecule in the vapour phase and in the crystalline state[75]. Analysis of the set of experimental data obtained enabled the authors[75] to suggest that the absorption frequency observed in the region of 61 cm^{-1} may be assigned to the $0,0 \rightarrow 2,2$ vibrational-rotational transition. The frequency ν_7 was found to be 22 cm^{-1} in contrast to the results of all previous studies. The new value of ν_7, obtained in the most accurate of the known investigations[75], throws doubt on the validity of the interpretation of the previous spectroscopic and electron diffraction data. It may be that one must resort to the concept of a strong vibronic interaction in the C_3O_2 molecule (the Jahn–Teller pseudoeffect) in order to eliminate the discrepancy observed between electron diffraction and spectroscopic data. At any rate, it appears desirable to repeat the electron diffraction and spectroscopic studies of the carbon suboxide molecule, the correct interpretation of which may serve as a key to the interpretation of the experimental data for many other molecules of different classes.

Among the electron diffraction studies where the experimental data were also interpreted from the standpoint of the quasi-linear model, mention should be made of the investigation of silyl isocyanate ($H_3Si-N=C=O$) and silyl thioisocyanate ($H_3Si-N=C=S$) molecules[76] as well as indium subselenide and subtelluride[77,78]. The usual harmonic approximation for the potential function of the deformation vibration of the silyl thioisocyanate skeleton agrees with experimental data, while for the silyl isocyanate molecule agreement with experiment is achieved using a potential of the type

$$V(\alpha) = -300\alpha^2 + 1090\alpha^4 \tag{8}$$

with minima at $\alpha_0 = \pm 28°$ and a barrier 20 cm^{-1} high at $\alpha = 0$.

An electron diffraction study of the high-temperature indium subselenide and subtelluride vapours[77,78] established that the deformation vibrations are described by the potential functions

$$V(\alpha) = 12816\alpha^4 - 3280\alpha^2 (In_2Se), \tag{9}$$

$$V(\alpha) = 18080\alpha^4 - 3376\alpha^2 (In_2Te). \tag{10}$$

The first function has minima at $\alpha_0 = \pm 21°$ and a barrier 210 cm^{-1} high at $\alpha = 0$. Analogous data were obtained also for the second function: $\alpha_0 = \pm 18°$ and a barrier 157 cm^{-1} high.

IV. BICYCLIC MOLECULES

Electron diffraction studies on bicyclo[2,2,2]octane[57] and triethylenediamine[79] showed that these molecules have a "quasi-D_{3h}" symmetry, i.e. there is a possibility of high-amplitude torsional vibrations about the C_3 axis (see Fig. 2). These vibrations are described satisfactorily by a potential function of the type

$$V(\Phi) = k_2\Phi^2 + k_4\Phi^4, \tag{11}$$

where Φ for the bicyclo[2,2,2]octane molecule is the dihedral angle between the C(1)C(2)C(3) and C(2)C(3)C(4) planes—the so called torsional angle. The potential for the triethylenediamine molecule has a similar form. The energy barriers in the torsional vibrations were found to be 35 cm^{-1} [57] and 30 cm^{-1} [79] for bicyclo[2,2,2]octane and triethylenediamine respectively, and the mean square values of the angle Φ are 12.8° and 11.0° respectively.

The electron diffraction data agree well with the results of X-ray diffraction studies on the same molecules[80,81]. The substitution of one hydrogen atom in bicyclo[2,2,2]-octane and triethylenediamine by a chlorine atom increases the barriers to 46.8 and 66.8 cm^{-1}, while the equilibrium angles Φ_e are respectively 16.2 and 16.4° according to the results of microwave studies on the above molecules[82,83].

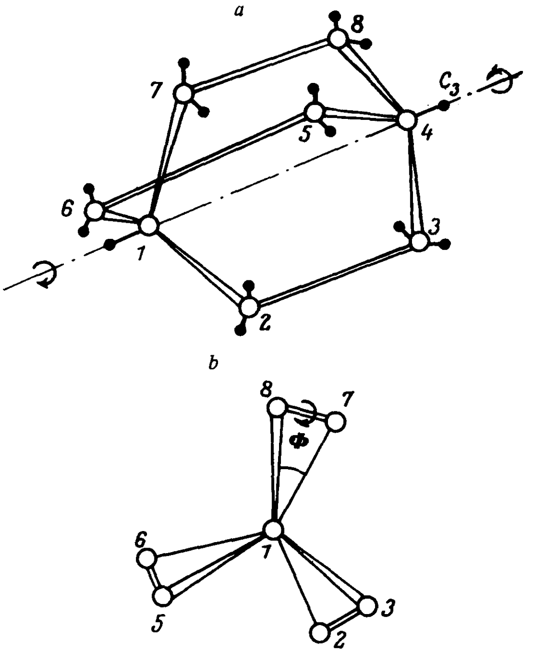

Figure 2. Torsional vibrations in the bicyclo[2,2,2]-octane molecule: *a*) configuration with D_3 ["quasi" – D_{3h}) symmetry; *b*) view along the C_3 axis.

V. ORGANIC MOLECULES WITH FIVE-MEMBERED RINGS AND INORGANIC HALIDES

1. Pseudorotation in Five-membered Rings of Organic Molecules

The concept of "pseudorotation" was introduced for the first time by Pitzer and coworkers[84–86] in order to account for the high entropy of gaseous cyclopentane. According to this concept, there is a continuous migration ("rotation") of the maximum deformation of the plane of the ring along the latter in the cyclopentane molecule and not simply out-of-plane vibrations. These vibrations represent the motion of the atomic nuclei without a significant contribution to the rotational moment of the molecule. The pseudorotation of five-membered rings is a more complex intramolecular motion than the deformation of linear molecules or torsional vibrations in bicyclic systems described above. This motion can be described by two vibrational coordinates, the phase Φ and the amplitude q of the pseudorotation linked by the expression

$$Z_j = \sqrt{\frac{2}{5}}\, q \cdot \cos\left[2\left(\frac{\pi}{5} j + \Phi\right)\right], \qquad (12)$$

where q is the deviation of the nucleus of the carbon atom from the plane (two-dimensional vibrational problem).

If it is assumed that the change in the coordinate q is described by the harmonic potential function

$$V(q) = \frac{k}{2}(q - q_0)^2 \qquad (13)$$

and that pseudorotation takes place virtually freely, it is possible to separate the motions along the two coordinates. Pitzer and coworkers[85] established on the basis of this approximation that $q_0 = 0.472$ Å for this molecule.

Further thermodynamic studies on cyclopentane[87-89] as well as semiempirical quantum-mechanical calculations of the energy of this compound[90-92] confirmed Pitzer's dynamic model. However, direct experimental confirmation of pseudorotation in cyclopentane was obtained for the first time in a study of the infrared spectrum of this compound[93]. The same workers[93] determined $q_0 = 0.479$ Å, which agrees well with the thermodynamic value found previously by Pitzer and coworkers[84-86].

According to modern ideas about the structure of five-membered rings, pseudorotation may be regarded as the superposition of two types of motion: the out-of-plane ring vibrations where one of the atoms is displaced from the plane (the "envelope" conformation with C_s symmetry) and torsional ring vibrations where two atoms are displaced simultaneously from the plane (the "half-chair" conformation with C_2 symmetry)[47,94] (Fig. 3). Pseudorotation can therefore be described as continuous transitions between configurations with C_2 and C_s symmetries (in all, ten configurations for each type of symmetry in a single pseudorotation cycle).

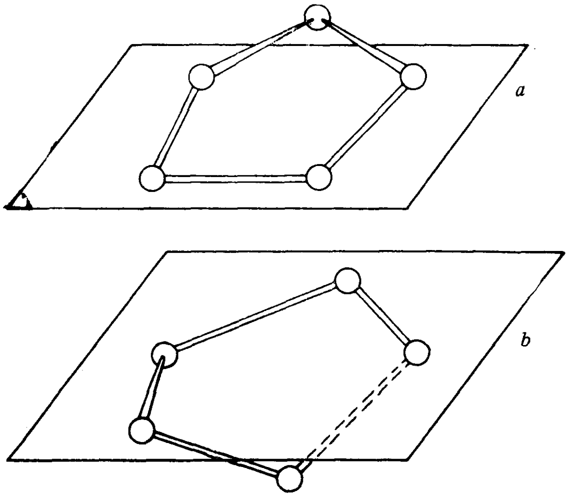

Figure 3. Conformations of five-membered cyclic molecules: *a*) "envelope" type (C_s symmetry); *b*) "half-chair" type (C_2 symmetry).

An electron diffraction study on cyclopentane[95] agreed fully with thermodynamic[84-86] and spectroscopic[93] studies and confirmed Pitzer's ideas concerning the complex motion of the nuclei in the molecule. However, the authors of the electron diffraction study[95] used a somewhat different dynamic model, where a vector S_j ($j = 1, 2, \ldots, 5$), defining the instantaneous position of a ring carbon atom, was introduced. During pseudorotation, each carbon atom moves in the vertical plane, passing through the given atom and the centre of the ring, the distance between the carbon atom and the centre of the ring being constant. Pseudorotation is also described by the two vibrational coordinates q and Φ, but in the given model the marked dependence of the C–C bond lengths on the displacement Z_j is eliminated. It was found that $q_g = 0.427$ for the effective displacement of the carbon atom from the plane (the subscript g denotes a value averaged with respect to temperature under the conditions of the electron diffraction experiment), which is somewhat less than the value obtained previously by Pitzer and coworkers[84-86] and in a spectroscopic study[93]. The equilibrium value $q_e = 0.438$ Å was also calculated[95] for the adopted anharmonicity constant of the out-of-plane vibrations $a = 2.0$ Å^{-1}. The difference between the values of q obtained in the electron diffraction[95] and spectroscopic[93] studies can be explained by the fact that the molecular parameters determined spectroscopically and by electron diffraction have a different physical significance (see, for example, Kuchitsu and Cyvin[6]).

Ab initio quantum-mechanical calculations on the cyclopentane molecule[96] confirmed the conclusion that the motion which depends on the angle Φ is virtually free and that $q_e = 0.43$ and 0.48 Å agrees well with the value determined by the electron diffraction method[95]. According to the authors' estimate[96], the height of the barrier separating the two configurations is in the range 4–8 kcal mole^{-1}.

Molecules containing a double bond [sic! a heteroatom?] in the five-membered ring have also been studied by electron diffraction: tetrahydrofuran[97-99], and 3-bromotetrahydrofuran[100]. In the first study[97], devoted to tetrahydrofuran and carried out at an earlier stage of the development of the electron diffraction method, only the planar model of the molecule was considered. A later investigation[98] established that the molecule has a non-planar structure. However, a satisfactory agreement between the theoretical and experimental intensity curves was not obtained for the individual models with C_s and C_2 symmetry (Fig. 3). Best agreement was achieved when the "envelope" and "half-chair" conformations were superimposed: $\alpha_1 C_s + \alpha_2 C_2$ (here α_1 and α_2 are the percentage contents of the forms with C_s and C_2 symmetry respectively) with $\alpha_1 \simeq \alpha_2$. This finding was interpreted[98] as evidence for the virtually free pseudorotation, the difference between the energies of the two conformers (C_s and C_2) being small and amounting to 0–3 kcal mole^{-1}.

A model of the pseudorotation of the five-membered ring, analogous to that used[95] for cyclopentane, was resorted to in an electron diffraction study[99] undertaken to interpret the experimental data for the tetrahydrofuran molecule. In this case too the model eliminates a marked dependence of the C–C and C–O bond lengths on the vibrational coordinates q and Φ. The average value of q_g was found to be 0.38 ± 0.02 Å, which is somewhat less than the spectroscopic value $q_0 = 0.470 \pm 0.025$ Å.[101]

Nevertheless one should note that the results of electron diffraction studies do not permit the conclusion whether or not the molecule is statically distorted or whether pseudorotation takes place in it. However, it has been established spectroscopically[48] that the C_2 form is energetically more favourable, while the C_s form has an energy higher by 1277 cm^{-1}.

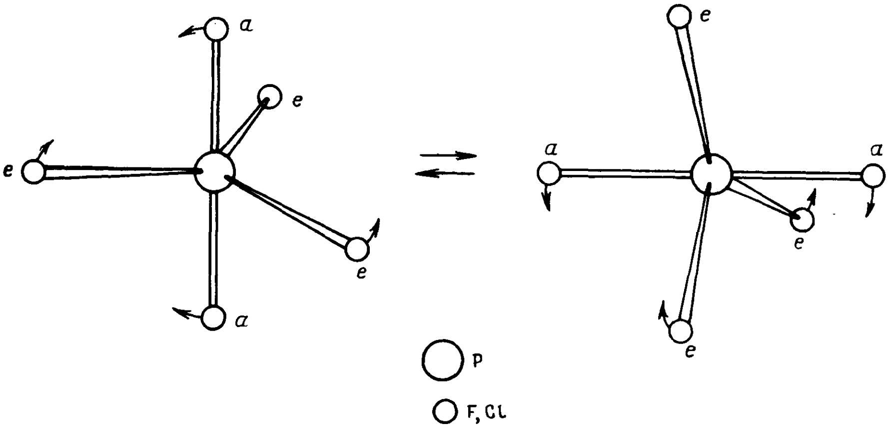

Figure 4. Schematic representation of the pseudorotation in the molecules of the phosphorus pentahalides PF_5 and PCl_5.

Apart from the electron diffraction determination of the molecular structure of 3-bromotetrahydrofuran, Smith et al.[100] also calculated the energies of its conformations by the Westheimer–Hendrickson method. They showed that the best agreement between the theoretical and experimental intensities is achieved on the hypothesis of almost free pseudorotation of the ring. The small energy differences between different conformations (of the order of 0.5 kcal mole^{-1}), found by conformational analysis, confirmed the results obtained by electron diffraction.

The electron diffraction data for other molecules with five-membered rings showed that the replacement of the oxygen atom by S, SiH_2, Se, CO, and GeH_2 leads to a greater stability of the C_2 form, the heteroatom or atomic group being displaced from the plane of the ring by approximately 20° during the vibrations[102]. The energy difference between the C_2 and C_s forms increases in the above sequence according to spectroscopic data[103-105].

2. Pseudorotation in Inorganic Halides

Pseudorotation in inorganic halides is a three-dimensional analogue of the high-amplitude intramolecular motion in five-membered cyclic organic molecules. Using these molecules as an example, it is possible to demonstrate that the characteristic duration of the experiment, which is different for different physicochemical methods used to study this problem (see Table), is significant for the observation of high-amplitude intramolecular motion.

An electron diffraction study of the PF_5 [106,107] and PCl_5 [107] molecules established that halogen atoms occupy two different positions—axial (*a*) and equatorial (*e*). The molecular model is described by the D_{3h} symmetry point group and the bond lengths $P-X(a) > P-X(e)$ (X = F or Cl). However, the NMR spectrum of PF_5 [108] indicates the complete equivalence of the fluorine atoms in the (*a*) and (*e*) positions, which served as the basis for the hypothesis of intramolecular exchange of fluorine atoms[14,109,110]. Analogous results have been obtained for the PCl_5 molecule[111-113]. The discrepancy between the electron diffraction and NMR measurements can be accounted for by the fact that the characteristic time of the NMR experiment (see Table) is apparently significantly longer than the time required for the exchange of fluorine atoms. Only the average picture of the intramolecular motion is therefore observed in this instance. On the other hand, it may be that the characteristic time of the electron diffraction experiment (see Table) is shorter than the exchange time of the halogen atoms. Because of this, at each instant the electron diffraction method records only the "instantaneous" picture of the scattering process in which halogen atoms occupy only the two most probable positions relative to the phosphorus atom, i.e. (*a*) and (*e*). For the same reason, the electron diffraction method cannot distinguish the possibilities involving the intramolecular motion in PF_5 and PCl_5 molecules as a result of which halogen atoms change places, on the one hand, or the static non-equivalence of the positions of these atoms, on the other.

Berry[109] and other workers[21-23,25,114-116] put forward the hypothesis that the exchange of axial and equatorial halogen atoms in phosphorus halides is a three-dimensional analogue of the pseudorotation in the five-membered rings of organic molecules (Fig. 4). Analysis of the Raman spectra of the PF_5 molecule in the gas phase made it possible to determine the pseudorotation barrier as 5.7 kcal mole^{-1}.[117]

As in phosphorus pentahalides, pseudorotation is observed in the heptafluorides of rhenium (ReF_7) and iodine (IF_7). The first electron diffraction study of the IF_7 molecule, carried out[118] using a visual method for estimating the electron scattering intensities, established that the nuclear configuration in this molecule is close to that of a pentagonal bipyramid (D_{5h} symmetry) in which five fluorine atoms are located in the equatorial plane, two fluorine atoms are on the axis, and the iodine atom is in the centre. According to LaVilla and Bauer[118], the fluorine atoms in the equatorial plane, which form a five-membered ring, are involved in a pseudorotatory motion, analogous to that described above for atoms in the rings of organic molecules.

The electron diffraction study of the IF_7 [119,120] and ReF_7 [119,121] molecules was repeated by Bartell and coworkers. Analysis of the results made it possible to establish reliably that the geometry of these molecules corresponds to the D_{5h} symmetry only approximately. Comparison of the theoretical intensity curve corresponding to the proposed model having D_{5h} symmetry with the experimental curve showed that the mean square vibration amplitudes for the non-bonded fluorine atoms

[$l_g(F_e\ldots F_e) = 0.254$ Å and $l_g(F_a\ldots F_e) = 0.236$ Å were obtained for ReF_7] are unduly high compared with the usually observed amplitudes for non-bonded pairs of atoms [cf. ReF_6 molecule[122]: $l_g(F_e\ldots F_e) \simeq l_g(F_a\ldots F_e) = 0.091$ Å].

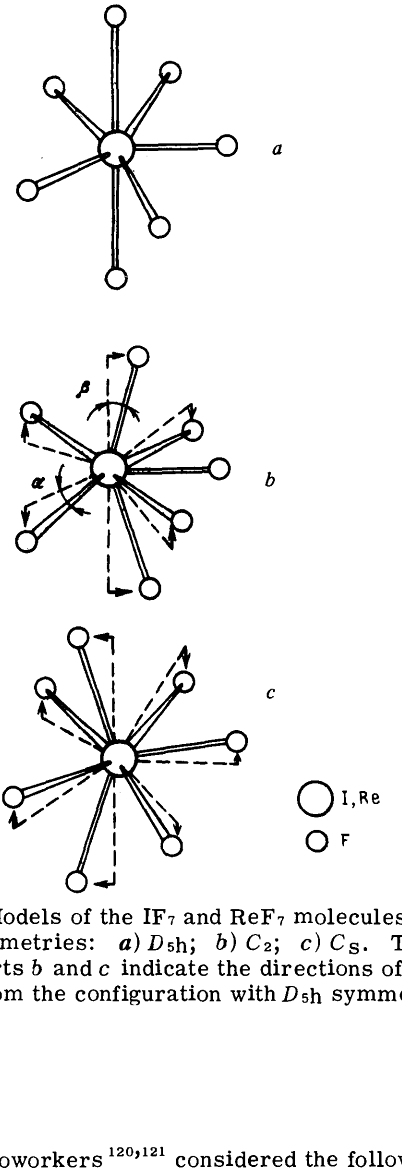

Figure 5. Models of the IF_7 and ReF_7 molecules with different symmetries: *a*) D_{5h}; *b*) C_2; *c*) C_s. The arrows in parts *b* and *c* indicate the directions of the deviations from the configuration with D_{5h} symmetry.

Bartell and coworkers[120,121] considered the following two alternative types of models of the IF_7 and ReF_7 molecules. In the first type static deformation is postulated—the displacement of fluorine atoms from the plane of the five-membered ring—described by the relation

$$\alpha_j = \alpha^0 \cos\left[2\left(\frac{2}{5}\pi j + \Phi_e\right)\right], \qquad (14)$$

$$j = 1, 2, \ldots, 5\ ,$$

where α^0 is the maximum angular deviation of fluorine atoms from the equatorial plane and Φ_e is the phase of the displacement of the same atoms. For $j = n\pi/10$ (n is an integer), we obtain a molecular model with C_s symmetry, while $j = (2n + 1)\pi/10$ yields a model with C_2 symmetry.

The angular displacement of the axial fluorine atoms is described by an analogous relation:

$$\beta_i = \beta^0 \cos\left[2\left(\frac{2}{5}\pi i + \Phi_a\right)\right], \qquad (15)$$

where β^0 is the maximum angular displacement of fluorine atoms from the C_5 axis, and Φ_a the phase of the displacement of the same atoms. From symmetry considerations, we have $\Phi_a = 4\Phi_e$. It was found that $\alpha^0 = 7.51$ and $\beta^0 = 4.55°$ for IF_7 and $\alpha^0 = 8.78$ and $\beta^0 = 7.65°$ for ReF_7. The molecular models are illustrated in Fig. 5. It is noteworthy that, both for models with C_s and C_2 symmetries and for their superposition $\alpha_1 C_s + \alpha_2 C_2$ with different statistical weighting factors α_1 and α_2, the factors governing the discrepancies between theoretical and experimental intensity curves proved to be fairly close, so that it was impossible to select any one of these models or their superposition.

The authors[120,121] put forward a dynamic pseudorotation model as the second possible interpretation of the experimental data for the ReF_7 and IF_7 molecules. It can be described as a continuous transition from the configuration with C_2 symmetry to one with C_s symmetry (Fig. 5). The motion of fluorine atoms in the equatorial plane is analogous to that on pseudorotation in the cyclopentane molecule. As a consequence of the strong interaction of vibrations of the e_2'' and e_1' type, the motion of the fluorine atoms in the equatorial plane is correlated with the motion of the axial atoms. Such interaction can be represented as the maximum "avoidance" of the fluorine atoms in the equatorial position involved in free pseudorotation by the axial fluorine atoms in the coordination sphere of the central atom.

Thus the electron diffraction method made it possible to establish unambiguously in this case also whether or not the observed distortion of the ReF_7 and IF_7 molecules is static, or whether a dynamic pseudorotation model is valid. However, the use of other experimental methods supports the dynamic model.

The effective dipole moment of the ReF_7 molecule, which increases as the temperature is reduced, has been observed by the method involving the deflection of the molecular beam in a homogeneous electric field[123]. A similar but less pronounced effect was found in the same study[123] also for the IF_7 molecule. These data, which disprove the quasi-rigid structure and demonstrate the temperature dependence of the results of the dipole moment measurements, support the dynamic stereochemically non-rigid molecular model. Furthermore, NMR studies of $Re^{19}F_7$ and $I^{19}F_7$ melts[124] indicate the complete equivalence to fluorine atoms in these compounds. Apart from the pseudorotation of the five-membered ring in these molecules, one may therefore also expect the occurrence of an intramolecular rearrangement leading to the exchange of the equatorial and axial fluorine atoms.

The study of the infrared and Raman spectra of IF_7[125,126] and ReF_7[125,127] supported a molecular model with D_{5h} symmetry. However, this does not conflict with the dynamic molecular model under consideration because an average pseudorotation pattern was apparently manifested in the spectroscopic experiment owing to the fact that its characteristic time (see Table) exceeds the time required for the intramolecular exchange.

Pseudorotation of a still more complex type may be postulated in the xenon hexafluoride molecule. The problem of the structure of this molecule has been discussed in a number of studies[128–131]. However, on the basis of theoretical analysis alone it was impossible to reach a conclusion about the molecular structure of XeF_6. X-Ray diffraction study did not permit the solution of the problem, because the compound does not form single crystals[132]. Spectroscopic investigations[133,134] likewise did not allow definite structural conclusions. The XeF_6 molecule was studied by electron diffraction several times[135–139]. A particularly detailed and thorough investigation was carried out by Bartell and Gavin[138,139] and their results are therefore described below.

The main conclusion which they reached[138,139] is that the molecular structure of XeF_6 in the gas phase cannot be described from the standpoint of a quasi-rigid model with O_h symmetry. Analysis of a wide variety of molecular models (O_h, C_{2v}, C_{3v}, D_{3d}, and C_s) and their linear combinations enabled them to establish that two alternative models may be reconciled with experimental data: (1) a static distortion model (with C_{2v}, C_{3v}, and C_s symmetry); (2) a dynamic model. According to the latter, the deformation vibrations with t_{1u} and t_{2g} symmetry in the XeF_6 molecule interact which leads to the correlation of the motions of the axial and equatorial fluorine atoms and to a distortion of the octahedron to give configurations with C_{2v}, C_{3v}, or C_{4v} symmetry. According to the authors[138,139], motion of this type can explain the virtual absence of an electrical dipole moment of the molecule[140,141] (the dipole moment measurements were performed by the method involving the deflection of a molecular beam by an inhomogeneous electric field), the unusual shapes, and anomalous half-widths of infrared absorption bands[130], as well as entropy data[142].

The nature of the dynamic distortions in the XeF_6 molecule can be clearly described by assuming that it resembles in some way three-dimensional pseudorotation in which fluorine atoms deviate from the octahedral positions by 5–10° as if striving to avoid certain regions in the coordination sphere of the Xe atom. In conformity with the Gillespie–Nyholm theory[143,144] (the theory of the repulsion of the electron pairs in the valence shell), the authors[138,139] identified these regions with the position of the lone electron pair of the Xe central atom, which migrates continuously in its coordination sphere from the position on the diagonal of the square formed by the equatorial fluorine atoms to the centres of the faces of the octahedra formed by one axial and two equatorial fluorine atoms (Fig. 6).

It is noteworthy that, although the idea of a stereochemically active lone electron pair does in general explain correctly the type of distortions in the molecule, nevertheless the theory of the repulsion of the electron pairs in the valence shell predicts much more pronounced distortions of the octahedron than are observed experimentally.

Claassen et al.[145] investigated the infrared, ultraviolet, and Raman spectra of XeF_6 in a matrix and in the gas phase, the Raman spectra and the spectra in the visible and ultraviolet regions being studied as a function of temperature. The authors suggest that, under the experimental conditions, the XeF_6 molecules exist in three electronic states ("electronic isomers"[148]): $^3A_{2u}$ (D_{3h} symmetry), ^3A_u or ^3B_u (C_{2v} symmetry), and A_{1g} (O_h symmetry). They showed[145] that all the spectra which they observed may be interpreted on the hypothesis of three "electronic isomers" of the XeF_6 molecule between which thermodynamic equilibrium is established in the course of approximately 10 min at 100°C. Evidently a reinterpretation of the electron diffraction data from the standpoint of the existence of the XeF_6 molecule in different electronic states is of undoubted interest. The interpretation of the molecular structure of XeF_6 in such a case requires in essence that one resorts to the Jahn–Teller pseudoeffect, since conditions under which the pseudoeffect is manifested may exist in the molecule[146–149].

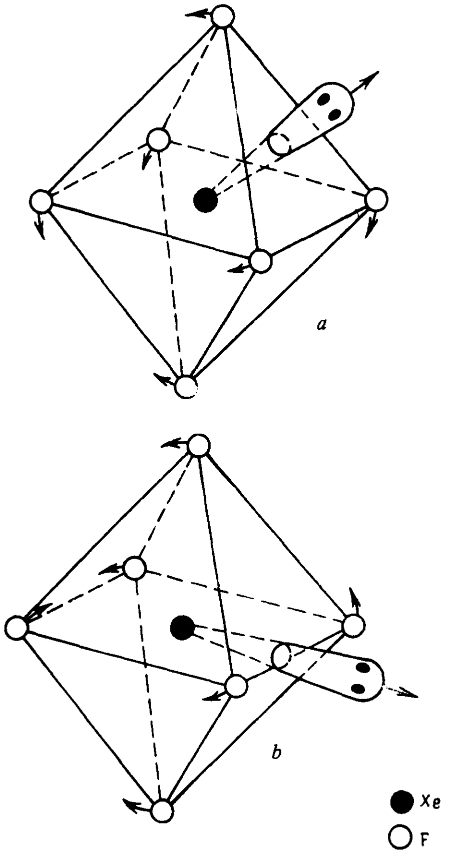

Figure 6. A model of the XeF_6 molecule. The possible positions of the lone electron pair on a face (*a*) and edge (*b*) of the octahedron and the directions of the distortions of the latter caused by the electron pair are shown.

The dynamic pseudorotation in the ReF_7, IF_7, and XeF_6 molecules described above should presumably be characterised by low frequencies. The following frequencies in the above molecules may be estimated from the electron diffraction data: 4.4 cm^{-1} (ReF_7); 5 cm^{-1} (IF_7); 10 cm^{-1} (XeF_6). Consequently the contribution of the pseudorotation to the thermodynamic functions of the given substances should be very considerable.

VI. JAHN–TELLER MOLECULES¶

Vanadium tetrachloride. The electron diffraction study of the VCl_4 molecule[150,151] was undertaken in order to determine its possible Jahn–Teller distortions, predicted on the basis of studies of the spectra of this compound[152–155] as well as theoretical calculations[45,156–160]. It was impossible to observe significant deviations of the VCl_4 structure from a regular tetrahedron[150,151], although, according to Morino and Uehara[150], the tetrahedron may deviate by 0.05 Å in the direction of the ν_2 stretching vibration. However, the greater amplitude of the vibrations of the Cl...Cl pair of nuclei in the VCl_4 molecule compared with $TiCl_4$ as well as certain other features of the structure and the vibrational spectrum of VCl_4 support, according to the authors[150], the operation of this effect. It appears that the Jahn–Teller distortions of the VCl_4 geometry are small and their measurement corresponds to the limit of the power of the modern electron diffraction method.

Vanadium hexacarbonyl. The molecules of vanadium and chromium hexacarbonyls have been investigated by electron diffraction[161]. Analysis of the experimental data established that the mean square vibration amplitudes of the vanadium atom in the $V(CO)_6$ molecule relative to the environment consisting of carbonyl groups are much higher than the corresponding values for the $Cr(CO)_6$ molecule. This was explained by the Jahn–Teller effect in the $V(CO)_6$ molecule. Schmidling[161] tested two types of models corresponding to the Jahn–Teller distortions of the nuclear configuration—of the E_g type (D_{4h} symmetry) and the T_{2g} type (D_{3d} symmetry). Best agreement was achieved for the model with D_{3d} symmetry and the deviation of the CO group in the direction towards the threefold axis was found to be 5.3°.

Rhenium hexafluoride. An electron diffraction study of the ReF_6 molecule established[122] that its geometrical configuration is described by the symmetry point group O_h. However, a spectroscopic study by Brand et al.[162] indicated the possibility of a Jahn–Teller distortion of this molecule, the displacement of the fluorine atom leading to trigonal (t_{2g} symmetry) distortions of the octahedron to the extent of 0.046 Å. The energy of the Jahn–Teller distortions was found to be 74 cm^{-1}. It is at present apparently difficult to explain the cause of the difference between the conclusions reached in the spectroscopic[162] and electron diffraction[122] studies. Nevertheless one may point out that Jacob and Bartell[122] observed a discrepancy between the theoretical and experimental intensities, which they were able to account for satisfactorily by the effects due to three-atom intramolecular scattering.

VII. BIS(CYCLOPENTADIENYL)BERYLLIUM

According to electron diffraction studies[163,164], the two cyclopentadiene rings in the $(C_5H_5)_2Be$ molecule are parallel to one another and mutually staggered, the distance between them being 3.375 ± 0.010 Å. The Be atom is located on a fivefold symmetry axis, which is the same as the two cyclopentadienyl groups, and can occupy two alternative positions at a distance $h_1 = 1.472 \pm 0.06$ Å from one ring and $h_2 = 1.903 \pm 0.008$ Å from the other.

It may be that the structural characteristics of this compound, observed in the electron diffraction experiment, are due to the manifestation of the Jahn–Teller pseudoeffect and that the beryllium atom oscillates between the cyclopentadiene rings along the fivefold symmetry axis. The potential curve describing such motion has two minima corresponding to different distances of the beryllium atom from the planes of the cyclopentadiene rings. This interpretation of the electron diffraction data[163,164] makes it possible to determine the "lifetime" of each configuration, which is 10^{-12}–10^{-13} s according to Ionov and Ionova[165], and the most probable barrier to the transition between the two configurations is in the range 1.4–2.9 kcal $mole^{-1}$.

VIII. MOLECULES OF OXYACID SALTS AND CERTAIN COMPLEX HALIDES

Electron diffraction studies on a number of alkali metal and thallium(I) metaborates[166–168], sulphates[169–171], chromates[169], perrhenates[172,173], molybdates[171,174], and nitrates[175–178] as well as complex compounds of the type $M^{I}M^{II}Hal_4$ [179–181] and M^{I} $^{II}Hal_3$ [182] (Hal = halogen and M^{I}, M^{II}, and M^{III} are Group I–III metals) yielded experimental data which have many characteristic features in common. In particular, it was observed that the electron diffraction patterns of these compounds contain only a limited amount of information about the position of the metal atom relative to the acid residue in molecules of the oxyacid salts and relative to the $M^{III}Hal_4$ (or $M^{II}Hal_3$) fragment in the complex compounds, revealed mainly in the region of low scattering angles. This situation is observed for both light and heavy atoms and cannot be explained simply by their low scattering capacity. A similar phenomenon has been called the "elution" effect[183]. It appears that it can be explained in many instances by an increase of the mean square vibration amplitudes of certain pairs of nuclei as a consequence of the increase in the populations of the excited vibrational levels of the molecule[183]. This appears to be a quite natural consequence of the influence of the high experimental temperature, particularly when the molecule executes low-frequency vibrations.

However, the above explanation, which is valid within the framework of the quasi-rigid molecular model, is inadequate for the salts of oxyacids and the complex compounds, because it is difficult to account for the above features of the experimental data simply by an increase in the populations of the excited vibrational levels. It appears much more natural to postulate a continuous change in molecular configuration as a result of the displacement of the metal atom relative to the quasi-rigid fragment (the acid residue, $M^{III}Hal_4$, or $M^{II}Hal_3$). Such a dynamic stereochemically non-rigid molecular model is apparently a general characteristic feature of the structures of many oxyacid salts and complex halides and

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¶ The classification of different types of high-amplitude motion employed in the present review is to a large extent arbitrary and is a result of the author's endeavour to reflect the main ideas, terminology, and explanations of the observed effects in the literature quoted. However, as already mentioned to some extent, the results of many of the studies of stereochemically non-rigid molecules discussed in Sections II–V may be accounted for on the hypothesis of a Jahn–Teller pseudoeffect in the molecules and the latter may be regarded as being of the Jahn–Teller type. This also applies to the exposition below.

possibly also other classes of compounds. We shall now consider the results of the electron diffraction studies in greater detail.

The electron diffraction patterns of alkali metal metaborates[166–168] in general correspond to the symmetrical linear BO_2 fragment and the low contribution to the overall scattering by the metal atom hinders the determination of its position. In electron diffraction studies on caesium[169,171], potassium[169], and thallium(I)[170,171] sulphates, potassium chromate[169], and thallium(I) nitrate[177,178], agreement between the experimental and theoretical density curves within the framework of a single quasi-rigid model can be achieved only for anomalously high vibration amplitudes of the metal atom relative to the oxygen atoms of the acid residue (l_g = 0.15–0.25 Å). The fragment of the acid residue then has a structure close to that of a regular tetrahedron for salts of the type M_2EO_4 (E = S or Cr; M = K, Cs, or Tl) or of an equilateral triangle in the case of thallium(I) nitrate (the non-equivalence of the angles at the central atom has been estimated[166–177] as ±5°, while the possible non-equivalence of the bond lengths does not exceed 0.1 Å). An electron diffraction study of the $TlNO_3$ molecule established[177] that best agreement between the theoretical and the experimental intensity curves is attained for a superposition of models of this molecule having different symmetries ($\alpha_1 C_s + \alpha_2 C_{2v} + \alpha_3 C_{3v}$) with the greatest contribution by the model with C_{2v} symmetry (α_2 = 71%).

Thus, in conformity with electron diffraction data, in the oxyacid salts quoted above there is a high symmetry of the acid residue in combination with a high mobility of the metal atom. This picture of the structures of many oxyacid salts has been confirmed by spectroscopic data. Thus studies of the infrared spectra of the vapours of the metaborates of certain elements[184–186] failed to detect the vibration frequency of the metal atom relative to the BO_2 fragment and the observed frequencies in the range 600 to 1940 cm^{-1} are due to the vibrations of the BO_2 group and were found to be almost independent of the metal atom to which the group is attached. Similar results, indicating a weak dependence of the NO_3 and SO_4 vibrations on the nature of the metal atom, were obtained also in studies of the infrared spectra of univalent metal nitrates in a matrix[187] and in the gas phase[188] and of univalent metal sulphates[189].

Virtually analogous results were obtained in electron diffraction studies on the $NaAlF_4$,[179] $KAlCl_4$,[180] $KYCl_4$, and $TlInCl_4$[181] molecules. It was established that the $MHal_4$ fragments in these compounds have a configuration close to that of a regular tetrahedron [within the limits of the errors in the measurements of the angles, which have been estimated[179–181] as ±5°, and the possible non-equivalence of the M^{III}–Hal bond lengths (<0.1 Å)]. The univalent metal atoms are located on a line perpendicular to one of the edges of the tetrahedron. An electron diffraction study of M^IBeF_3 molecules (M^I = Na or K)[182] showed that the BeF_3 fragment has a configuration close to that of an equilaterial triangle and that the metal atom is located within the plane of the triangle on a line perpendicular to one of its sides. A characteristic feature of the studies on complex salts of both types is anomalously high vibration amplitudes of the metal atom relative to the quasi-rigid $M^{III}Hal_4$ or $M^{II}Hal_3$ fragment (for example, 0.19 Å in $TlInCl_4$[181]). This makes it possible to treat the observed configurations as the most probable and the molecular structures of these compounds should be described with the aid of a dynamic stereochemically non-rigid molecular model, fully analogous to the model discussed above in relation to oxyacid salts.

The results of *ab initio* quantum-chemical calculations on the LiNC molecule by Clementi and coworkers[190,191], *ab initio* calculations on the $LiBO_2$ molecule[102], calculations by the LCAO-MO semiempirical method on the $LiNO_3$ and $TlNO_3$ molecules[193], as well as calculations on the dependence of the electrostatic energy of the interaction between the cation and anion on the spatial position of the metal ion for $CsNO_3$ and $TlReO_4$ molecules, carried out[194] using an ionic model (Fig. 7), are of undoubted interest in connection with the problem under consideration.

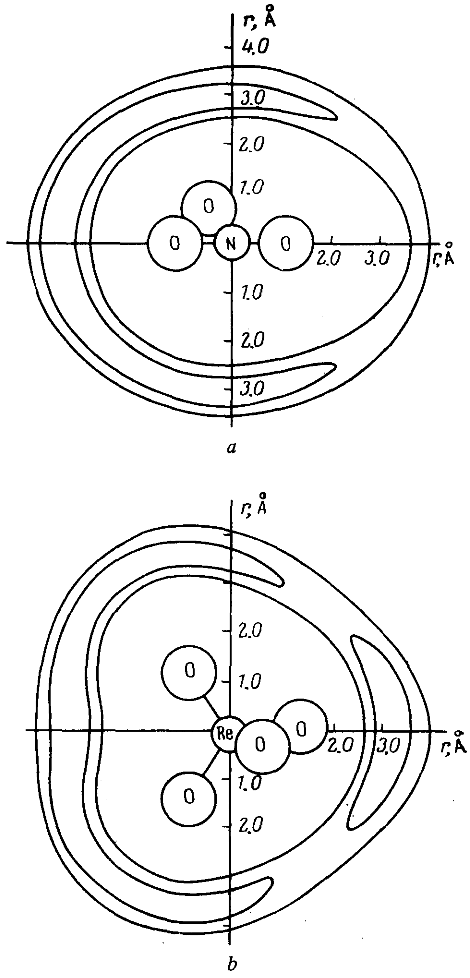

Figure 7. A map of the potential energy surface for the motion of the metal atom relative to the acid residue: *a*) $CsNO_3$; *b*) $TlReO_4$.

The electronic structure of the LiNC molecule has been calculated[191] for different positions of the metal atom relative to the NC fragment. The calculated maps of the energy surfaces for the motion of the Li atom showed that there is virtually no energy barrier between the Li–C≡N and Li–N≡C configurations. On thermal excitation (energy about 0.3 eV), the Li atom rotates freely about the NC group.

Virtually analogous results were obtained also in quantum-chemical calculations on $LiBO_2$ [192] and $TlNO_3$ [193] molecules.

Thus the results of quantum-chemical calculations have fully confirmed the conclusions reached in electron diffraction studies concerning the stereochemical non-rigidity of the molecules of many oxyacid salts.

This exhausts, for the present, the list of electron diffraction studies in which experimental data were clearly interpreted from the standpoint of the stereochemically non-rigid molecular model. However, one cannot rule out the possibility that experimental studies on many organic and inorganic compounds, in the explanation of the results of which a quasi-rigid molecular model has been used, can also be interpreted from the standpoint of the stereochemically non-rigid molecular model.

IX. CONCLUSION

The extensive experimental electron diffraction data available at the present time have shown, in agreement with the results derived by other physicochemical methods, that complex nuclear motions are executed in molecules of different classes, namely high-amplitude motions. They lead to important chemical consequences.

In the first place this concerns the classical ideas about the geometrical configurations of molecules and their symmetry. The classical structural theory is based in essence on the coordinates of the minima in a multidimensional potential energy surface, whose set forms a fixed geometrical configuration with a definite point symmetry, and not on physically determined spatial positions of the nuclei in the molecule. Therefore, if a nucleus in the molecule executes a high-amplitude motion, then under certain conditions (see Section II) the positions of the potential energy minima lose the significance of the spatial characteristics of the nuclear system and the molecular structure cannot be described, in principle, by a time-invariant geometrical configuration with fixed positions of the nuclei (and its point symmetry). In this case only the solution of the corresponding wave equation for the motion of the nuclei (if necessary, taking into account non-adiabatic corrections) and the determination of the probability density function for the distribution of the nuclei yields an adequate (although not unduly clear) picture of the structure. With the aid of this function, it is possible, in principle, to calculate the probability of any location of the nuclei. In this connection one must mention Liehr's study [36], where the quasi-rigid molecular model was subjected to a serious criticism and an attempt was made to develop a more general approach to the description of nuclear subsystems, including the construction of the complete potential energy surface.

The next problem which must be considered concerns the nature of the chemical bond in stereochemically non-rigid molecules. We shall examine it in relation to salts of oxyacids and complexes. It was shown above that in molecules of these compounds there is virtually free rotation of the metal atom about the acid residue or the $M^{III}Hal_4$ and $M^{II}Hal_3$ fragments. This shows that the theory of the chemical bond, in particular the theory of directional valence, is unsuitable for the description of the electronic structures of these molecules.

A specific feature of the chemical bond involving the metal atom in the compounds under consideration is its delocalisation in the molecule—its dynamic, distributed nature. This is not a bond between any pair of atoms, but a bond formed by the metal atom with the acid residue (or the $M^{III}Hal_4$ and $M^{II}Hal_3$ fragments) as a whole. In order to stress this feature of the bond, Clementi [191] suggested that it be called a polytopic bond and that the molecules containing such bonds should also be referred to as "polytopic" molecules. The nature of the polytopic bond is apparently close to that of the bond in ionic crystals, where there is also no appreciable bond directionality.

Another characteristic feature of the chemical bond under consideration consists in the relatively weak distorting influence of the metal atom on the acid residue (or $M^{III}Hal_4$ and $M^{II}Hal_3$ fragments), which is a consequence of the migration of the metal atom. However, according to thermodynamic studies (see, for example, Cubicciotti [195]), there are no grounds for the assumption that this bond is energetically weak and that the corresponding molecule is thermally unstable.

We may note that the experimental and theoretical studies which have been carried out have in essence merely posed the problem of polytopic bonds and that the multiplicity of questions which have arisen still require an answer. For example, the elucidation of the role of vibronic interactions in high-amplitude motions may be regarded as a problem of this kind. If the vibronic interaction is intense, the electronic spectra of molecules cannot be treated separately from nuclear motion, which leads to the necessity for a radical revision of the ideas about the nature of the chemical bond.

The accumulation of experimental data on stereochemically non-rigid molecules is important also for many other chemical problems. Thus tunnelling effects play an appreciable role in the kinetics of chemical reactions, particularly at low temperatures. The problem was formulated for the first time by Bourgin in 1929 [196] and was analysed in detail theoretically in a number of other studies [197–200]. Pearson [201] attempted to regard the activation energies of uni- and bi-molecular reactions on the basis of the analysis of the orbital symmetries of the electronic states of the molecules involved in the reaction and the influence of close excited electronic states. This approach is extremely important for the understanding of the mechanisms of intramolecular rearrangements.

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Structure of Amorphous Polymers

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A critical survey is made of experimental results obtained by the application of direct structural methods—X-ray, electron, and neutron diffraction, electron microscopy, and several other physical methods—to amorphous linear polymers. A list of 162 references is included.

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I. INTRODUCTION

For many years research workers have paid steady attention to the structure of polymers at a supermolecular level. Special progress has been made in studying the structure of crystallising polymers—the folding of polymeric molecules, detected originally in thin films[1] and in single crystals[2-4]—which was very reliably transferred also to crystallites present in blocks and in the fibres of most polymers[5-7]. A wide range of supermolecular crystalline structures has been discovered and studied in detail[5-7], and a systematic classification has been developed[8].

Less attention has been paid to the structure of amorphous polymers, firstly because of the opinion that polymers in the amorphous state were structureless, and secondly because application of the usual structural methods

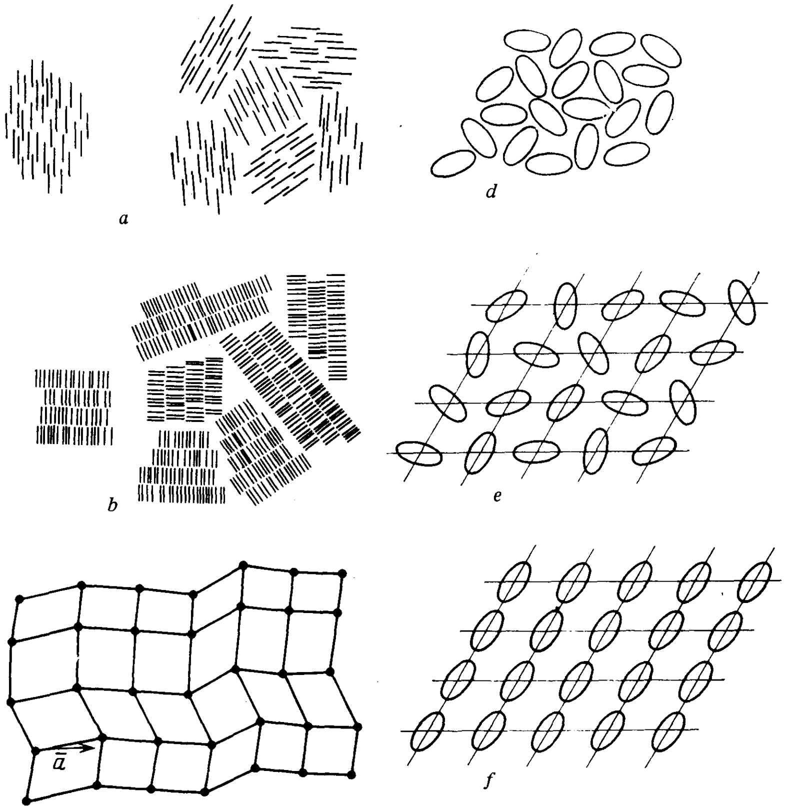

Figure 1. Schemes of packing of rod-shaped molecules: *a*) nematic structure; *b*) smectic structure (according to Friedel); *c*) ideal paracrystalline lattice (according to Hosemann); *d*) liquid packing of cross-sections of macromolecules; *e*) gasocrystalline; *f*) crystalline (according to Kitaigorodskii).

to amorphous substances yielded little information. Systematic study of the structure of amorphous polymers was initiated in 1957 by the work of Kargin et al.,[9] whose underlying idea, as expressed by one of the authors 17 years later[10], was that the structure of a polymer in the amorphous state should be similar to its structure in the crystalline state. Although the bundle model of the structure of amorphous polymers, in the form in which it was presented in that[9] and other publications of these workers[11,12], is now regarded as unsatisfactory, the actual concept of a high degree of structural order permeates the majority of current models of the amorphous state.

The present Review traces the main trends and results in the experimental study of the structure of amorphous polymers, and the extent of agreement with the most generally accepted current models of the amorphous state.

II. NOMENCLATURE OF STRUCTURES OF DIFFERENT DEGREES OF ORDER

A multitude of organic compounds exist in Nature that, over a certain temperature range, are intermediate between liquids and crystals with respect to the degree of molecular order and hence physical properties[13,14]. They comprise elongated molecules, and for this reason are able to form molecular aggregates with different degrees of ordering. The structure and the properties of liquid crystals have now been investigated for more than half a century, so that almost the whole terminology used to describe non-crystalline packages of macromolecules was developed for liquid crystals.

All types of intermediate ordering were generally termed "mesophases" (from *mesos*—intermediate and *phasis*—phase) or "mesomorphs", the "mesomorphic" state. In 1933 Rinne suggested for one- and two-dimensional mesophases, in contrast to a three-dimensional crystalline phase, the term "paracrystal", thereby emphasising that the majority of liquid crystals are *para*-substituted benzene derivatives. Somewhat earlier, in 1922, Friedel had independently suggested the term "nematic mesophase" (from *nematos*—fibrous, filamentous) for a unidimentional mesophase, and "smectic" for a two-dimensional mesophase. These structures are shown diagrammatically in Fig. 1*a*, *b*.

These terms already came to be applied in the same sense to analysing polymer structures in the early papers of the 1930s.[15] The term "paracrystal" was then made more specific by Hosemann in 1950 in his paracrystalline model of the structure of polymers as a whole, including regions of all degrees of order[16,17]. This worker postulated the presence of a three-dimensional lattice in the arrangement of atoms in a polymer, with all three parameters of the unit cell not constant but conforming to some coordination statistics (Fig. 1*c*). The type of statistics and the consequent lattice disturbances are determined by the degree of molecular order—from liquid to monocrystalline—in different polymers or in different portions of the same polymer.

In 1959 Kitaigorodskii proposed[18] the new term "gasocrystalline" structure for certain highly ordered nematic and smectic forms. If the axes of the long molecules are located at the points of a regular (crystalline) two-dimensional hexagonal lattice and the molecules perform random ("gaseous") rotations about their axes, a model of the gasocrystalline state is obtained (Fig. 1*e*). This structure will exhibit a nematic or a smectic character according as neighbouring molecules undergo random or coordinated displacements respectively.

In 1963 Vainshtein[19] discussed in the greatest detail possible types of aggregates of chain molecules. The simplest and most natural organisation of chain molecules into three-dimensional aggregates, also satisfying the principle of densest packing[20], was taken to be a parallel arrangement with a varying degree of order and with the parallelism maintained in varying degree. Having placed the chain molecule with its axis passing through a branch point of one of the five possible ideal two-dimensional networks (Fig. 2*a*, *b*), this author then examined every type of disturbance of the initial position of this molecule, various combinations of which are summarised by the scheme in Fig. 2*c*. Thus the structure of a given polymer can be regarded as established when the type of aggregation of chain molecules to which the given structure corresponds has been found experimentally and the quantitative characteristics of the disturbances involved have been determined. Later in the monograph[19] theoretical consideration was given to the character of the X-ray diffraction from all types of aggregates of chain molecules, the results being illustrated by optical diffractograms from models or X-ray diffraction patterns of model materials.

III. CLASSICAL STRUCTURE ANALYSIS OF AMORPHOUS POLYMERS

Application of X-ray diffraction to the study of natural and synthetic polymers began immediately on the appearance of industrial equipment for structural analysis. Most of the polymers known at that time were amorphous, so that greater attention was then paid to their structure than at the present time, with the abundance of well crystallised polymers, more suitable for study by means of X-rays.

Firstly the X-ray patterns of monomers and corresponding polymers were compared[15]. The greatest differences were observed with polymers having large side-chains—poly(methyl acrylate), poly(vinyl acetate)—polystyrene, polycarbonate, polyindene—whose patterns exhibited two halos within a certain range of angles, whereas the corresponding monomers showed only one of them. The additional halo, always having the greater periodicity, was termed a "polymerisation ring". The reason for its appearance became clear when it was observed to contract on to the equator in the case of an oriented specimen (Fig. 3*c*). In the uniaxial stretching of a polymer the axes of the macromolecules are oriented preferentially in the direction of stretching, and therefore the equatorial reflection may be governed merely by the interchain distance. At the same time a good correlation was noted between the length of the side-chain and the periodicity of the equatorial reflection[21]. The fact that a "polymerisation ring"—or "intermolecular interference", as it came to be called later—is observed even in an isotropic specimen shows that the polymer molecules in a block are not randomly entangled but are arranged in parallel in microregions, each randomly oriented relative to its neighbour. In the terminology of liquid crystals such polymers have a nematic mesomorphous structure.

These ideas were developed as early as 1936, when Katz published his review[15], but they were forgotten during the postwar years, when the centre of gravity of structural investigations was transferred to well-crystallised stereoregular polymers. Experimental results gradually began to accumulate afresh: in 1950 Pritshk[22] demonstrated four

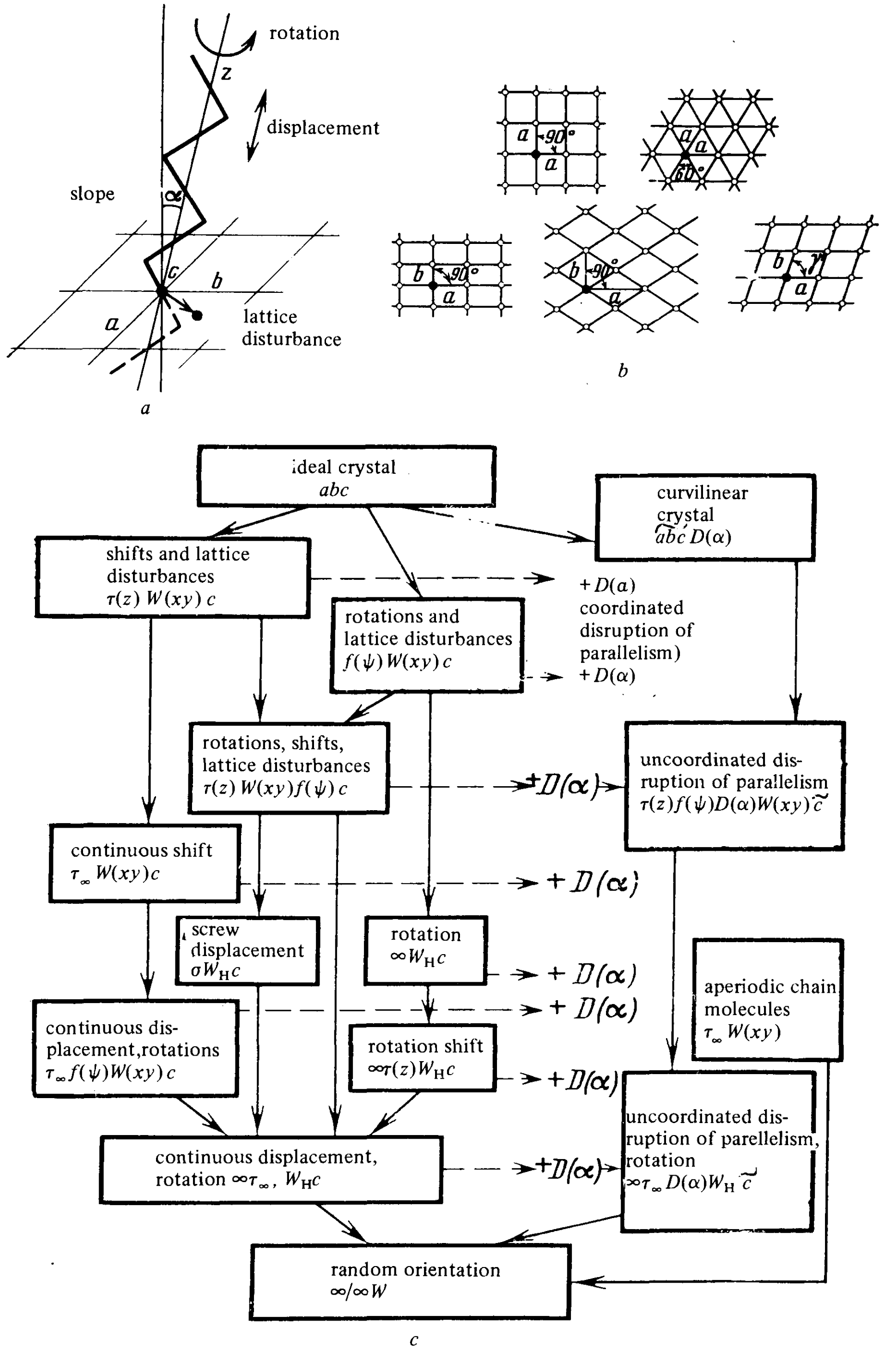

Figure 2. Packing of chain molecules (according to Vainshtein): *a*) types of disturbance of ideal packing; *b*) five regular two-dimensional networks; *c*) types of aggregation of chain molecules.

types of X-ray patterns obtainable with nylon-6, which he attributed to various combinations of liquid-amorphous, nematic, smectic, and crystalline structures; in 1951 Krimm and Tobolsky[23] reproduced the texture of atactic polystyrene discovered by Katz and Fuller during the 1930s; and in 1959 Kitaigorodskii[20] directed attention to polyacrylonitrile as the clearest example of a polymer having a gasocrystalline structure[18] (Fig. 3*a*). A nematic type of structure was noted in molten and amorphised specimens of poly(vinyl chloride)[24,25], poly(vinylidene chloride)[26], their copolymers, and chlorinated poly(vinyl chloride)[25]. The smectic state of isotactic polypropylene was revealed by X-ray diffraction and dilatometrically[26,27]. The accumulation of experimental data was accompanied by attempts to systematise mesomorphous polymeric structures. For example, Ruscher distinguished seven different types of ordering of chain molecules[28]—amorphous, nematic, smectic, nematic–hexagonal, smectic–hexagonal, defect-crystalline, and ideally crystalline structures.

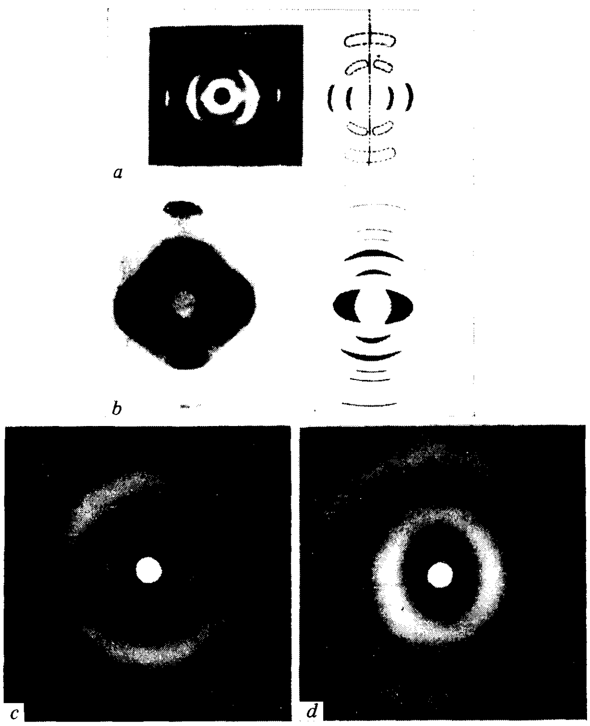

Figure 3. Effects of ordering on X-ray patterns of oriented amorphous polymers: *a*) two-dimensional long-range order[17] (gasocrystalline structure[18]) in polyacrylonitrile; *b*) one-dimensional long-range order in poly(ethylene terephthalate)[40]; *c*) interchain short-range order in polystyrene; *d*) as (*c*) in poly(methyl methacrylate).

As noted above, a rigorous and full classification of possible types of packing of chain molecules was given by Vainshtein[19]. Since the beginning of the 1970s increasing numbers of publications have appeared on the application to polymers of the analysis of radial distribution curves of electron density based on the dependence of the X-ray intensity on the scattering angle (or based on the potential distribution in the scattering of electrons). A comparatively large amount of structural information—interatomic distances in molecules, number of closest neighbours (coordination number), their mean distance, etc.—is given by radial distribution curves in the case of amorphous substances of low molecular weight[29]. For example, the examination of short-range order in cycloalkanes enables the molecular conformation (chair and boat forms of cyclohexane over different temperature ranges, the W form of cyclo-octane) and a coordination number of ~ 11.5 to be established[29] from the observed intramolecular distances. The molecules of n-alkanes, however, were packed in the liquid like cylinders of rotation, with a mean distance of 5.6 Å between their axes[29] and ~ 6 nearest neighbours.

The greatest difficulties in analysing radial distribution curves are encountered in separating the contributions of intramolecular and intermolecular interference. This is probably why such analysis was first applied to atactic polystyrene[30] and its *para*-halogenated derivatives[31], for with this polymer, as we have already seen[15,23], the effects of intra- and inter-molecular interference are quite sharply separated even on the initial scattering curves. The statistical mean intrachain short-range order was found to be the same as in isotactic polystyrene, which has since been confirmed independently by nuclear magnetic resonance[31]. Among intermolecular distances, benzene rings in neighbouring chains were 5 Å apart, and their axes 9–11 Å apart.

This method has been used to investigate a large number of molten crystalline polymers—polyethylene[33,34], polychlorotrifluoroethylene, poly(ethylene sebacate), gutta-percha[34], natural rubbers from various sources[35,36], polyacrylonitrile[36], and polycarbonate[37]—by Ovchinnikov and his coworkers, who employed the set of interchain distances in the crystal lattices of the polymers to separate the maxima observed on the radial distribution difference curves into intramolecular and intermolecular. The general deduction for all the polymers was that the character of the short-range order in the melt corresponded to their structure in the crystalline state: i.e. a parallel arrangement of chain segments and their packing in the basal plane analogous to crystals (square, rectangular, hexagonal) are present also in molten crystalline polymers. In several cases transitions are observed from one type of packing to another: in molten polyethylene a change from rectangular (rhombic) to hexagonal packing was observed at 175–200°C,[36] and in polybutadiene one pseudohexagonal packing passed into another at ~ 75°C.[36] The number of intermolecular maxima on the difference radial distribution curve was regarded as a relative measure of the degree of perfection of the short-range order and the size of the ordered regions. Most frequently there were two, corresponding to regions of diameter ~ 25–30 Å, but sometimes three (polyacrylonitrile[36]) or one (gutta-percha[34]). Other workers[38] have obtained a similar result by this method for polycarbonate [bisphenol A polycarbonate]: the size of ordered regions for an amorphous specimen prepared by injection moulding, and also after annealing below the glass point (at 120°C for 3 h), was 20–30 Å, but after prolonged annealing above this point (at 190°C for 122 h) the size had increased to 50–60 Å.

Nevertheless, the ambiguity inherent in the separation of contributions by intramolecular and intermolecular scattering to the maxima on the radial distribution curves makes a different interpretation of the experimental results possible. Thus Fischer et al.[39] have attempted to assign all the maxima on the radial distribution curves of polyethylene to intrachain distances.

The difficulties in interpreting the X-ray patterns of amorphous polymers made theoretical consideration of this question necessary. A general solution of the problem of the diffraction of X-rays on amorphous polymers has not yet been found, but certain limiting or simple cases can be examined theoretically, and hence the main features of the X-ray patterns actually obtained from amorphous polymers can be predicted and explained[19].

The first noteworthy result is the character of the diffraction pattern to be expected with non-parallel packing of the chain molecules. The pattern of scattering should be saw-tooth in character: at scattering angles corresponding to the repeat period of the chain a sharp jump in intensity should be observed, followed by a slow fall. This applies even to 8 units in a linear chain segment. Such a pattern of scattering does not correspond to the experimental X-ray photographs. Further consideration of the diffraction from an individual curved macromolecule showed[19] that the periodicity should appear with oriented preparations as a single meridional reflection, but with isotropic specimens as a ring at the same angle of scattering. The effective chain segment with respect to diffraction is then 6–7 units long. A second effect in diffraction from a single curved chain is gaseous or liquid intramolecular scattering. If large side-groups are absent, this scattering should be apparent as a uniformly decaying background. If the monomer unit has a complicated structure, the intramolecular scattering will be characterised by diffuse maxima, as with molecular gases and liquids.

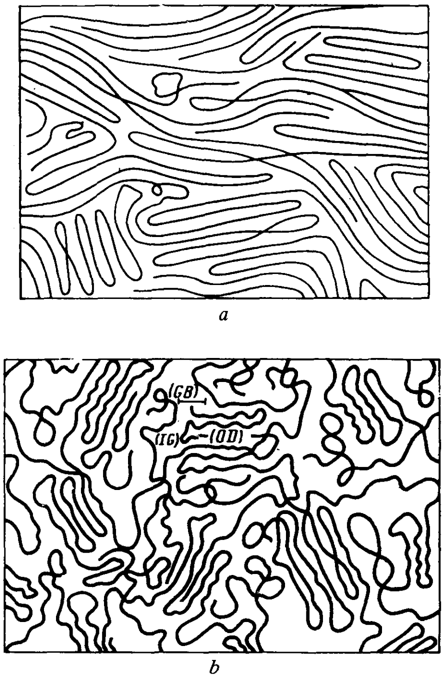

Figure 4. Diagrammatic representations of structure of amorphous linear polymers: *a*) Vainshtein model[19]; *b*) Jeh–Geil model[103,107].

Parallel packing, as far as possible, is also advantageous in aggregates of curved chains[19]: portions with skew contacts between neighbouring molecules make hardly any contribution to the overall interference pattern, whereas portions with an approximately parallel arrangement of chains will give a new diffraction effect, consisting in the appearance of an interference spot on the equator of an oriented specimen (or an additional ring, in comparison with the scattering from a single chain, with an isotropic specimen). The presence of displacements and rotations of chains does not prevent the appearance of an equatorial reflection, and the spread in interchain distances merely results in blurring of this reflection. Qualitative estimates of the size of the interference region give 20–40 Å.

Thus three types of diffraction effects must be expected on the X-ray patterns from amorphous polymers (they can be reliably separated only in the case of oriented specimens)[19]—(i) a maximum (or maxima) on the meridian resulting from chemical periodicity in the chain molecule, (ii) a maximum on the equator as a consequence of interchain interference of roughly parallel chain segments, and (iii) a diffuse background of intramolecular scattering, with "liquid" maxima when the monomer unit is complicated in structure—all of which are in some measure apparent on the X-ray patterns of amorphous polymers, especially clearly with amorphous biopolymers (see Figs. 217 and 218 in the monograph[19]) but less distinctly with synthetic polymers owing to the considerably greater non-uniformity of molecular mass, branching, stereoregularity, and other characteristics. Examples of amorphous textures with meridional reflections are incompletely crystallised oriented poly(ethylene terephthalate)[40] (Fig. 3*b*) and fibres of certain polyamino-acids[41]; amorphous textures with equatorial reflections are exhibited by polystyrene[15,23], poly(vinyl acetate)[15], and poly(vinyl chloride)[26]. If intramolecular and intermolecular interferences greatly overlap, the X-ray patterns exhibit a tendency for one ring (usually the inner ring) to contract to an equator, and the other ring to a meridian, which occurs e.g. with a polycarbonate[42] and with poly(methyl methacrylate)[45] (Fig. 3*d*).

Thus the present-day possibilities of the theory and practice of classical structural analysis enable amorphous polymers to be regarded[19] as comprising (Fig. 4*a*) regions of 20–40 Å with roughly parallel packing of segments of macromolecules. A given molecule may pass through several regions or (if strongly bent) may enter the same region several times. "Skew" contacts are present between molecules in intermediate zones. Models in which the structure of an amorphous polymer is represented by bundles of macromolecules in which good or approximate parallelism of the molecules extends to a considerable length—or conversely by disordered microtangles each formed by a single molecule—cannot explain the observed character of the X-ray patterns[19]. The possibility of the chain folding is not excluded in the model illustrated by Fig. 4*a*, although it is not considered a decisive cause of the formation of regions with a parallel arrangement of chain segments.

IV. RESULTS OF ELECTRON MICROSCOPY

When considering the results of electron-microscopic investigations, we must bear in mind that electron beams interact with an object according to laws different from those governing the scattering of light[44]. A source of error in interpreting electron micrographs lies in so called artefacts, a term which is usually taken to imply peculiarities of the image that are due not to the structure of the object but to the method of preparing the specimen. Several typical examples of artefacts can be found in monographs on the technique of electron microscopy[44], and others will be noted below in connection with the results of the electron-microscopic study of the structure of amorphous polymers.

All publications concerned with the present topic can be arbitrarily divided, according to their specific purpose, into three groups. The first group comprises studies whose principal or subsidiary aim was to detect individual macromolecules on the electron micrographs. As early as 1940 Husemann and Ruska had reported[45] the presence of spherical particles of diameter 150–300 Å in specimens of iodinated glycogen, in good agreement with the calculated diameter of 240 Å for a molecular coil of the given molecular mass and macroscopic density. Spherical domains, roughly comparable with a single macromolecule, were later detected on micrographs of thin films from solutions of polystyrene[46–48], poly(methyl methacrylate)[46–48], and natural rubber[49].

The range of objects was expanded by using replicas from "brittle" fractures and ultrathin sections from block specimens. These methods have revealed, for example, two scales of dimensions in the observed structures—molecular of diameter 40–80 Å in poly(methyl methacrylate)[50] and 150–200 Å in melamine–formaldehyde resins[51] as well as in polyacrylonitrile[52]; and micellar of diameter 200–800 Å in poly(methyl methacrylate)[50,53], 700–900 Å in phenol–formaldehyde[42] and melamine–formaldehyde[51] resins [and in phenolic, dioctyl phthalate, epoxy, leached epoxy, and silicone resins[54]], and 200–840 A in polyacrylonitrile[53]—but recently the method of replicas from "brittle" fractures has been severely criticised[55–57]. Thus even at the temperature of liquid nitrogen cleavage is non-brittle: because of local heating the polymer may undergo deformation under conditions of either forced elasticity, rubberlike elasticity, or viscous flow. Furthermore, experimental facts have been found[58] contradicting the initial assumption that a cleavage fracture bends the supermolecular structures. Thus the morphology recorded on replicas represents the actual process of fracture of the material, not the three-dimensional structure of the polymer.

With regard to the spherical particles observed in thin films mainly the interpretation of the results has changed. Thus Schoon et al.,[59,60] who investigated thin films (~ 100 Å) of polystyrene, poly(methyl methacrylate), butadiene–styrene copolymers, and also silicone replicas from these films, using several methods for comparing both films and replicas, and plasticising the polymers with various solvents, showed that two scales of spherical structures are actually observed, but no exact correspondence with the dimensions of individual molecules was established. They determined particle-size distribution curves from micrographs of narrow fractions of the polymers, and demonstrated that the first scale of particle diameters (47–62 Å for $M = (1-7) \times 10^5$ in polystyrene, 40–60 Å for $M = (2-70) \times 10^5$ in poly(methyl methacrylate), and 70 Å for $M = 10^5$ in the copolymer) are substantially smaller than the dimensions of a molecular coil of a polymer of the same molecular mass having the given macroscopic density. The second scale of particle diameters, representing aggregates of particles of the first range, exceed the calculated diameter of a single molecule by factors of 2–9. We shall return to the present interpretation of these results when discussing the third group of publications.

Observation of individual molecules under an electron microscope requires more complicated and rigorous procedures. For example, Richardson[61,62] used the vacuum sputtering of very dilute (~ 10^{-4}%) solutions of polymers—polystyrene, polyacrylonitrile, poly(methyl methacrylate), poly(vinyl acetate), etc.—in mixtures of a solvent with a precipitant in certain proportions. With very high molecular masses ($\gtrsim 10^6$), when the application of traditional methods is very difficult, electron microscopy is able, with a correct approach to problems of preparation, to cope successfully with the measurement of both the molecular mass and its distribution[63].

The second and largest group of publications on the electron-microscopic study of the structure of amorphous polymers is the product of research workers of Kargin's school, and has been the subject of several detailed reviews[11,64–68]. These studies were directed mainly at detecting experimentally the spontaneous ordering of micromolecules even in the case of non-crystallising polymers.

For this purpose a search was originally made for model substances differing in chain flexibility, and type of inter- and intra-molecular interaction (sometimes of exotic character), such as arsenic polymers (salvarsan)[68], polyacrylic acid[69], fluorinated and silicone rubbers[70], copolymers of the diethyl ether complex of vinylphosphinic acid with acrylic acid[71], etc. Application to such compounds of the usual preparation techniques (mostly film formation from dilute solutions) revealed two main types of organisation—globules, containing more than one coiled macromolecule, and fibrils (bundles of extended macromolecules). In several cases the latter were able to aggregate further to form regular polyhedra (methyl methacrylate–acrylate copolymer[68]) and well developed dendrites (copolymer of diethyl ether complex of vinylphosphinic acid and acrylic acid[71]). The so called "banded structures" were recognised as the most typical secondary formation, with such methods of preparation, from bundles of chains in any amorphous polymer.

The next stage was to study the structure of polymer solutions[67]. This complicated task involved the use or redevelopment of special techniques, such as one-step replicas from fractures of vitrified solutions[73], dissolving the polymer in a solvent at a temperature above its critical point (propane, colophony, ammonia) and "firing" the solution in a vacuum on to a support[74], thermal attachment[75,76]. Application of these methods to polymers differing in chain flexibility—e.g. in the sequence polystyrene, polyacrylonitrile, acetylcellulose, poly-(γ-benzyl glutamate)—showed that flexible molecules (polystyrene) do not form fibrils, whereas with rigid chains, as in poly-(γ-benzyl glutamate), the spontaneous aggregation of macromolecules in solution can be attacked only by special procedures. In the case of polymers having chains of intermediate rigidity (polyacrylonitrile and acetylcellulose) either globular particles (containing several dozen macromolecules) or fibrillar formations may appear depending on the ratio of solvent to precipitant.

It must be admitted that the structural studies of the Kargin school were treated with reserve by foreign workers[5,77], who remarked that "more detailed photomicrographs and electron micrographs of globules and bundles were absolutely essential" as proof of the results[5]. A tendency to reinterpret electron-microscopic data from several previous studies has recently begun to appear even in papers by Soviet investigators [sic][60]. It has been suggested[58], for example, that the "banded structures", which had been considered one of the main structural forms in amorphous polymers[65], should be regarded as artefacts of the preparative processes, since no diffraction data have yet been obtained that would support their presence in the bulk of a polymer. The appearance of images of such morphology on photomicrographs is attributed to wrinkling of the preparations under the influence of surface tension[58]. No confirmation has yet been obtained in other laboratories of the observation of large faceted structures in amorphous polyacrylic acid[68] and its copolymers with the ether complex of vinylphosphinic acid[71], as also the detection of spherulites by Utsuo and Stein in industrial poly(vinyl chloride)[78] and by Natov[79] in atactic poly(methyl methacrylate) with 3% of poly(ethylene adipate). The absence from these papers of diffraction data casts doubt on the reality of such structures in amorphous polymers. Cases are known in which the authors themselves find a simpler explanation for the observations: thus the coarse crystalline formations in annealed gels of poly(vinyl chloride) with dioctyl phthalate[80] proved to be crystals of phthalic acid, a degradation product of the plasticiser[81].

In order to eliminate the influence of the surface relief of films, fractures, and cross-sections, which is an indication of the preparative processes rather than the structure of the material, several methods were proposed and have been used to etch the surface layers[56,82-88]. Although application of the "mildest" of them[83-86] to crystalline materials has little effect on the character of the images obtained[56], a radical change in the pattern is observed in several cases with amorphous polymers. Instead of the spherulitic formations often detected on replicas from fractures in amorphous polymers, e.g. polyurethane rubber[56] or poly(methyl methacrylate)[89] (arising, as is now understood, from the mutual intersection of the propagation fronts of fracture cracks), a globular morphology is observed in both cases after surface layers of the cleavage have vaporised in the gas-discharge plasma[56,90]. Still more surprising and unexpected is the transition from the clearly defined fibrillar morphology of replicas from cleavage planes of highly oriented specimens of poly(methyl methacrylate)[91] to the globular morphology of replicas from etched surfaces of cleavage planes in analogous specimens[90].

In the search for objective criteria of the correctness of an interpretation of electron-micrographs obtained from crystallisable polymers it was proposed that optical diffraction patterns should be compared with small-angle X-ray patterns[92] or with diffractograms obtained from block specimens in polarised light[60]. The diffuse character of small-angle X-ray patterns and optical diffractograms from amorphous polymers makes wide application of this test to amorphous preparations difficult, although it may prove useful in several cases. Fig. 5 gives electron-microscopic and optical diffraction results obtained by various workers for uniaxially oriented specimens of atactic poly(methyl methacrylate). The replicas of oriented films after being etched in the gas discharge exhibit globular formations and their aggregates of dimensions 200–2000 Å (*a* and *b*) with a somewhat distorted form when specimens are stretched at temperatures above the glass point[90]. The axial ratio of such particles was always appreciably smaller than the macroscopic degree of stretch if preparation was undertaken after removal of the stretching force, but corresponded to it when the load was maintained. The attempt to compare the Fraunhofer diffraction from a photomicrograph with the X-ray pattern of oriented poly(methyl methacrylate) at large scattering angles[58] (*c*) contradicts the very idea of the method of analysis of photomicrographs and is pointless. On the other hand, the "rhomboid" pattern obtained when polarised light is scattered by the specimen[93] (*f*), analogous to the scattering pattern for a set of anisotropic cylinders[93] (*e*), corresponds more closely to the fibrillar morphology found on replicas of unetched fractures (*d*). Results obtained[94] for isotropic and oriented amorphous films of poly(ethylene terephthalate) subjected to oxygen etching contrast with those for etched oriented poly(methyl methacrylate). An unoriented preparation reveals only globular formations of diameter 300–400 Å, but oriented specimens (amorphous texture[40]) exhibit elongated structural units 100–200 Å wide and up to 1 μm long.

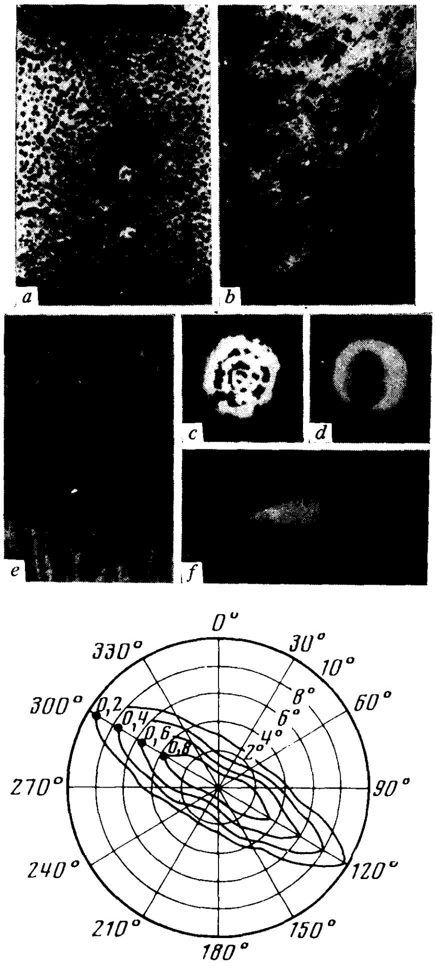

Figure 5. Morphology and diffraction of oriented poly(methyl methacrylate): *a*) electron-micrograph of replica from cleavage plane of 400% drawn polymer after ionic etching (magnification × 7000)[56,90]; *b*) as (*a*) × 70 000; *c*) Fraunhofer diffractogram from micrograph (*a*)[58]; *d*) X-ray large-angle diffraction pattern of block specimen[58,90]; *e*) micrograph of replica from cleavage plane without etching[91]; *f*) diffractogram obtained with polarised H_V light for polymer specimen stretched by 700%; *g*) theoretical intensity distribution of polarised light scattered by a set of anisotropic cylinders[8,93].

Hence the inclusion of ionic etching in the preparation of electron-microscopic objects eliminated the artefacts of the "brittle" cleavage method and of film formation from dilute solutions, but at the same time introduced new artefacts, probably due to uncontrolled heating of the surface layer[95] and to the inadequately studied mechanism of polymer degradation under ion bombardment[96]. At the present time this method shows great promise for investigation of the phase morphology of multicomponent polymer systems, such as polymer and filler[97,98], mixtures of polymers[99,100], cross-linked systems[101], etc.

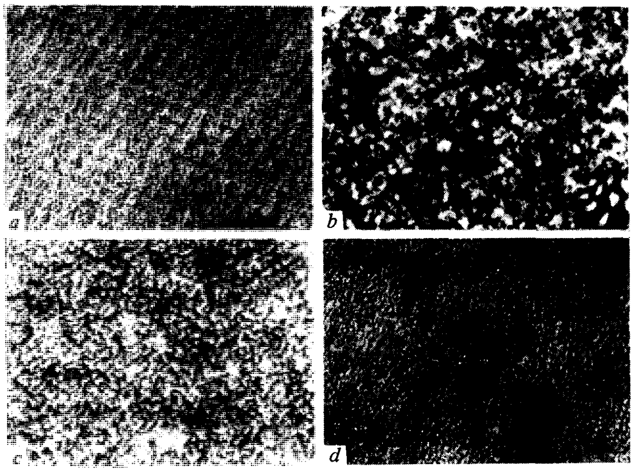

Figure 6. Granular (nodular, domainal) morphology of films of amorphous linear polymers: *a*) bright-field electron-micrograph of biaxially oriented (2 × 2 ×) amorphous film of poly(ethylene terephthalate) (shadowed with platinum plus carbon)[104]; *b*) dark-field micrograph of film of natural rubber[108]; *c*) bright-field micrograph of poly(methyl methacrylate) film (contrast enhancement with UO_2)[60]; *d*) as (*c*) (phase contrast)[115].

We have thus approached the third group of publications, reported the most complete utilisation of the current arsenal of aids to electron microscopy on preparations varying widely in their previous thermophysical history. Chronologically the first paper in this series was that by Frank et al.,[102] in which ionic etching revealed the granular structure of polycarbonate films. Grains of diameter < 100 Å were observed in films quenched in ice-water from a state of rubberlike elasticity (160°C); they could be enlarged reversibly to 200–900 Å by annealing at 110°C (glass point 150°C), and brought back to the previous size by being quenched again. The reversible character of the changes during the anneal–quench cycles, and the abrupt change in mechanical losses for an unannealed specimen in the region of 100°C, evident on the temperature curve of $\tan\delta_{\mathrm{mech}}$, indicated the structural nature of this phenomenon.

Efforts by research workers of the Geil school soon detected granular structures (nodal, nodular, domainal) in amorphous specimens of poly(ethylene terephthalate)[103-104] (Fig. 6*a*), polycarbonate[105], polystyrene[106], and natural rubber[107,108]. Usually the granular structure (grain size 60–100 Å) was revealed simply by shadowing the films, so that artefacts were tested for by such well known procedures as iodination[104], contrast intensification with osmium tetroxide[108], various types of heat-treatment[103-111], uni- and bi-axial orientation[105,103,108], analysis of crystalline morphology developed from controlled variation of the nodular structure[103-105,108], and also chemical etching[109,110].

The application to amorphous polymers of dark-field microscopy[103,106,107]—a standard method applied to crystalline substances[44], including crystalline polymers[87,104,108]—represented a fresh advance in their electron microscopy. By tilting the illuminating system of the microscope to an angle corresponding to the Bragg angle of the inner amorphous halo of the polymer it is possible to obtain an image of the object by means of those electrons that are responsible for the appearance on the electron-micrograph of the segment of the diffuse ring that has passed through the aperture diaphragm. But it is known that inner halos on diffraction patterns of amorphous polymers are due mainly to intermolecular interference of parallel chain segments. As a consequence we might expect that bright spots would appear on the dark background of the micrographs, these representing ordered regions in which the axes of the macromolecules were perpendicular to the radius of the chosen segment of the diffraction maximum[109]. Dark-field micrographs of thin films (< 500 Å[109]) of poly(ethylene terephthalate)[103], polystyrene, and natural rubber[108] (Fig. 6*b*) exhibit discrete bright spots respectively 75, 27 ± 13, and 20 Å (30 Å[109]) in size. Bright-field (unshadowed) micrographs of poly(ethylene terephthalate) films revealed a nodular structure of the same dimensions[103,109], those of polystyrene showed little contrast, and with films of natural rubber aggregates of grains of diameter 100–150 Å were probably observed after shadowing with platinum[108]. A more definite tendency for grains to aggregate into superdomains was traced by another novel method—decoration with gold—in poly(ethylene terephthalate) during uniaxial and biaxial orientation[104]: the primary grains of 60–100 Å were aggregated into coarser superdomains of minimum size 300–500 Å, which behaved as individual entities during orientation. We can now recall the studies by Schoon[59,60] discussed already, in which the application of various methods for intensifying contrast also revealed in polystyrene, poly(methyl methacrylate), and butadiene–styrene copolymer films grains and their aggregates respectively 40–70 and 200–900 Å in size (Fig. 6*c*).

The granular morphology of amorphous films has been observed many times on bright-field micrographs even without any intensification of contrast—in the films of collodion[44,109] and polyvinyl formal resin[109] used as supports, in thin films of poly(ethylene terephthalate)[103] and poly(methyl methacrylate)[111], and also in thin amorphous inorganic specimens of silicon dioxide[112,113] and germanium dioxide[114]. In general it was clear that phase contrast is not the final factor in establishing such a morphology on the micrographs, and such effects have usually been regarded rather as undesirable phenomena[44,109].

A recent publication[115] traces in greater detail the influence of phase contrast on formation of the electron-microscopic image in work with amorphous subjects in the range of limiting magnifications. The authors consider[115] that phase contrast can and must be converted from an interfering factor into an effective new procedure in electron microscopy applied to polymeric subjects, as it was[116] when the structure of inorganic materials was examined at limiting resolutions. The main conclusion from the experimental work[115] was that phase contrast is able to reveal in amorphous poly(methyl methacrylate) films (100–150 Å thick) grain-like structures of diameter 15–30 Å and their linear aggregation with a periodicity of 15–40 Å extending for 100–200 Å (Fig. 6*d*).

Such an abundance of well founded electron-microscopic data on nodal structures in amorphous polymers led to the model of the latter described in detail by Yeh[107], shown diagrammatically in Fig. 4*b* with his lettering. The actual grains observed on bright-field micrographs are usually $G = 40–100$ Å in size. The central portion of the grain $OD = 20–40$ Å comprises more or less parallel and almost equidistant chain segments, and is revealed in dark-field electron microscopy. The boundary regions of the grains, 10–20 Å thick, include folds, chain ends, and individual bent chains. The intergranular regions, of size 10–50 Å, consist of intermediate portions of chains of individual molecules (probably oligomeric) and free space. The refinement of this model by Klement and Geil[104] involves merely introducing a supergranular structure (supernodes, superdomains), within which intergranular bonds are assumed to be denser than those between grains in different superdomains; however, these authors do not indicate the reason for such differentiation of intergranular bonds. It was assumed[107] that the grains should have directional properties; polymer chains may enter and leave the ends of grains, so that the latter should be linked as in a string of beads. Nevertheless, the possibility that they could be linked into a three-dimensional lattice is not denied.

The "electron-microscopic" and "diffraction" structural models of the amorphous state of polymers (suggested independently though not simultaneously) are clearly very similar (Figs. 4*b* and 4*a*). Such similarity is evidently due to the use of essentially the same experimental diffraction evidence of order in the arrangement of chain segments in the amorphous state. The contribution of electron microscopy to further development of the model was to detect boundaries between regions of nematic order and disorder, and to establish more detailed size characteristics independently of diffraction estimates. The authors of the electron-microscopic model could cite no experimental evidence for the underlying hypothesis that macromolecules had a predominantly folded conformation in the ordered regions. They considered that the hypothetical chain folding in grains was supported by the facts that the crystallisation of poly(ethylene terephthalate) involves the conversion of grains of size 75 Å into isometric crystallites of size 140 Å, in which the chains probably have a folded conformation[104], that polycoumarin grains of size 60–110 Å coalesce during prolonged annealing at the glass point to form platelike crystals, chain folding in which has been proved by electron diffraction[105], and that the nodal morphology of natural rubber films of size 100–150 Å is transformed on cooling into a lamellar morphology with plates 55 Å thick in the direction of the chain[106].

V. OTHER PHYSICAL METHODS OF INVESTIGATION

The low degree of order in the arrangement of segments of macromolecules in amorphous polymers and the small size of the ordered regions make it necessary to use the widest possible range of physical methods to study structural details of the amorphous state. Definite progress has already been made in this direction, and several interesting facts have been discovered concerning the supermolecular organisation of amorphous polymers. Simple density measurements on an amorphous polymer, e.g. poly(methyl methacrylate)[117,118], showing a decrease on quenching from the rubberlike elastic state and a continuous increase during annealing below the glass point, have already indicated the occurrence and the reversibility of ordering in the amorphous state, while the proportionality of the density of oriented specimens of the same polymer to the double refraction[118] indicates quite clearly the character of the ordering.

However, this method is not always sufficiently sensitive: in the case of polystyrene, for example, the density remains constant after it has been stretched 50 times[119], although the double refraction and the infrared dichroism definitely record a certain degree of molecular orientation[120]. It is noteworthy that oriented amorphous preparations have seldom been chosen as subjects for structural investigations. The above examples may be supplemented by the observation of a long period (150–250 Å) on the equator of the small-angle X-ray diffraction pattern of slightly oriented poly(vinyl acetate)[121]. Furthermore, application of X-ray diffraction and physicomechanical study of oriented amorphous fibres of polyaminoacids has shown[41] that the modulus of elasticity calculated from the change in the repeat distance along the chain under the influence of tension is several times larger than the macroscopic value for the specimen as a whole. By analogy with the corresponding phenomenon in crystalline polymers, which has been studied thoroughly, this result may indicate an alternation along the texture axis of regions differing in degree of order.

More comprehensive information has been obtained for isotropic specimens. Thermographic study has shown that ordering processes, unconnected with crystallisation, the effects of which appear separately[125–127], occur in the amorphous phase of poly(ethylene terephthalate)[117], poly(vinyl chloride), and copolymers of the latter[122–124] during annealing. Interesting attempts have been made to apply nuclear magnetic resonance to polyethylene in concentrated solutions and in the melt[128]. The distortion of the form of the resonance line observed in the spectra of these preparations were interpreted as due to the superposition of two components, narrow and wide, which they assigned to disordered and ordered regions respectively. The amorphous phase of polyethylene was similarly divided into two components on analysis of the n.m.r. spectrum obtained by rotation at the "magic" angle[129], although the numerical ratios found[129] for the two components differ from the values obtained by other workers[128]. The development of order in amorphous polymers is apparent in the infrared spectra[130]: the splitting of the carbonyl vibrational band is similar in character when amorphous poly(methyl methacrylate) is precipitated from solution or from a polymerisation product and when poly-ε-caprolactone is crystallised from the melt. The type of splitting indicates the presence of mutually oriented molecular structures in poly(methyl methacrylate).

The scattering of light has recently been used to examine the structure of amorphous polymers. With poly(methyl methacrylate)[39], polystyrene[131], and polycarbonate[39] the observed intensity of vertically polarised scattering exceeded the calculated value, which may be due to the presence of scattering centres of 1000–2000 Å.[39] The intensity of this scattering increases with rise in temperature, but the monotonic character of the dependence does not change on passing through the glass point[131], as might have been expected from the electron-microscopic observations[102,109]. The horizontally polarised component of the scattered light was independent both of temperature and of angle of scattering[39,131]. This was regarded[39,131] as implying that the internal structure of the scattering centres is isotropic: i.e. the method of light scattering reveals no anisotropy in the molecular packing at dimensions exceeding 1000 Å.

Another approach to solving the problem of the scattering of light on poly(methyl methacrylate) is to replace the latter by a model consisting of spheres having different refractive indices[132]. The histograms ultimately obtained (which showed the relative contents of hypothetical spheres having various refractive indices) were even sensitive to annealing and quenching of the specimen. Nevertheless, attempts to confer a real physical meaning on absolute values of the density calculated from the refractive indices obtained are hardly soundly based. Indeed, the values found[132]—a content of ~ 40% of spheres of density $\rho_{calc} = 1.29$ g cm^{-3}—appear very high in comparison with $\rho_{amorph} = 1.19$ and $\rho_{cryst} = 1.22$–1.23 g cm^{-3},[5] especially in view of results obtained by application of small-angle X-ray scattering to amorphous materials.

Theory indicates[133] that the intensity of the scattering of X-rays at very small angles by a material exhibiting density fluctuations extending over the range 10–10^4 Å is directly proportional to the square of the density difference between "particle" and medium and to the number of inhomogeneities, and is related exponentially to their radius of gyration. For a long time, therefore, it was expected that papers would appear on the application of such scattering to the study of amorphous polymers, in order to obtain experimental estimates of the density difference between domains and interdomainal space. The very low intensity of small-angle scattering by amorphous polymers was already emphasised in the first few papers[117,134]. Within the limits of the moderate resolving power of the apparatus used ($2\theta \geqslant 8.5'$) the experimental curves for poly(ethylene terephthalate) were well reproduced by Guinier's approximation[133] with a radius of gyration of the inhomogeneous regions of 15–20 Å.[134,135] This was half the radius of domains found from electron-microscopic measurements[56,109]. It was noted that annealing at a temperature below the glass point tends to increase the product of the number of scattering centres and the square of the density difference. A study by small-angle X-ray scattering of the crystallisation of the same polymer has revealed[136] a decrease in density of uncrystallised regions from 1.337 to 1.31 g cm^{-3} (by 1.5%) with increase in the degree of crystallinity to its maximum value.

Lin and Kramer[137] were probably the first to attempt to estimate the density difference between domains and interdomainal space directly from absolute measurements of the intensity of small-angle X-ray scattering: for polycarbonate they found the radius of gyration of inhomogeneities to be 130 Å, and the density difference to be 1.6–1.8% (it is noteworthy that $\rho_{cryst} - \rho_{amorph} = 21\%$). Polycarbonate was soon examined with small-angle apparatus of ultrahigh resolution[138] ($2\theta_{min} = 10''$). The intensity of scattering at moderately small angles ($2\theta > 20'$) was almost constant, and consistent with the theoretical scattering on density fluctuations in a homogeneous liquid. At angles approaching the smallest possible with the given apparatus the intensity of scattering increased sharply, and could not be described in Guinier coordinates by a single radius of gyration. Hence it is not possible to calculate both the density difference and the concentration of scattering centres from the experimental data. If the density of the domains is taken to be ρ_{cryst}, their dimensions will lie in the range 50–3000 Å, while the volume fraction is ~ 0.04%. This most likely comprises dust particles, catalyst residues, etc. If, however, the volume fraction and the dimensions are taken from electron-microscopic data (~ 50% and 50–100 Å respectively), the density of the domains should be very close to that of the matrix. Similar results have been obtained for poly(methyl methacrylate)[39] and for polyglycol ethers[101]. Thus the results of small-angle X-ray scattering indicate a very insignificant difference ($\leqslant 1.5\%$) in the density of inhomogeneities in the structure of amorphous polymers.

A new page in research on the structure of amorphous polymers was opened by Krigbaum and Goodwin[139], who used small-angle scattering by specially prepared specimens to determine the size of single macromolecules in the block state. They studied the scattering of X-rays by a 5% solid solution in ordinary polystyrene of polystyrene molecules weighted at the ends with silver atoms. The calculated root mean square distance between the silver atoms, i.e. between the ends of the chain, was 269 Å, which exceeded by 24% the unperturbed dimensions of macromolecules of the given molecular mass (217 Å for $M = 87\,000$) according to Flory[140].

Polymer*	$10^{-3}M_w$	R_w(bl), Å	$R_w(\theta)_{calc}$[135], Å	$\frac{R_w(bl)-R_w(\theta)}{R_w(\theta)}$, %	$\frac{R_w(bl)}{M_w^{1/2}}$
ps	7.1	30[142]	23.1	21.2	0.33
ps	21	40[143]	39.7	0.8	0.28
ps	57	80[143]	65.3	22.5	0.34
ps	90	100[143]	82.1	21.8	0.30
ps	97	90[145]	85.1	5.4	0.29
ps	112	115[143]	91.5	25.7	0.35
ps	325	200[143]	156	28.2	0.35
ps	390	280[145]	258	8.5	0.30
pmma	250	116—130[146—148]	109[146]	16—19	—
pe	81	126[39]	123[39]	24.4	—

* ps = polystyrene; pmma = poly(methyl methacrylate); pe = polyethylene.

The small-angle scattering of neutrons by solid solutions comprising a low concentration of deuterated molecules dissolved in the usual substance, or conversely, has become more widely used during recent years. Most of the investigations have been made on polystyrene[141-145], as well as on poly(methyl methacrylate)[146-148] and molten polyethylene[39]. The radius of gyration of the macromolecules in the block R_w(bl) was in all cases comparable with values for solutions in a θ solvent $R_w(\theta)$, but nevertheless usually exceeded it on the average by 20%, as is evident from the Table. The latter shows clearly for polystyrene the proportionality of the size of macromolecules in the block to the square root of the molecular mass: $R_w(bl) = \frac{1}{3}M_w^{1/2}$. A similar dependence has been found also for poly(methyl methacrylate)[148].

The possibility of obtaining quantitative information on the dimensions of macromolecules in the block, demonstrated in the above publications, is undoubtedly one of the greatest achievements of polymer science during recent years. Nevertheless, the conclusions reached by the authors and sustained by such authorities as Fischer[39] and Flory[162], on the correspondence of the conformation of macromolecules in the block and in solution, which were based merely on the correspondence of their external dimensions, are too categorical in the Reviewer's opinion.

In the search for ways of resolving the apparent contradiction between many facts on the development of order in the packing of macromolecules and their coiled form several authors sought to deepen the analogy between amorphous and crystalline structures: it was suggested that macromolecules are folded in vitreous polymers. This hypothesis was probably first put forward by Robertson[149], the immediate occasion being his comparison of experimental density ratios for several polymers in crystalline and amorphous states with those calculated for various angles between neighbouring chain segments. The best agreement was observed if divergence of the segments from parallelism did not exceed 5–15° for different polymers. However, Robertson's calculations on the density of packing of molecules with skew contacts have recently been subjected to serious criticism. According to Fischer et al.[39] the density of packing of polyethylene calculated on the assumption of a random distribution of angles of contact between neighbouring segments is 0.687, whereas experimental values for the molten and vitreous states are respectively 0.625 and 0.645.

Despite the controversial character of the initial premise, the hypothesis of chain folding in the amorphous state gained wide popularity. Details were filled in by Privalko et al.,[150] who suggested a formula for calculating the length of a fold from experimental values of the molecular mass, the steric factor of restricted internal rotation, and the cross-section of the molecules. An active search is being made for experimental evidence of the folding of chains in the amorphous state. Thus small-angle meridional reflections have been observed in several crystallisable polymers even when, according to large-angle X-ray diffraction, crystallisation has not yet taken place[151]. Petermann and Gleiter[152] observed that, if a single crystal of polyethylene in which the axes of folded chains are parallel to the electron beam is melted directly in the electron microscope, the diffuse ring of period 2.55 Å is absent from the resulting electron-diffraction pattern. This means that even after fusion the axes of the macromolecules retain their previous orientation perpendicular to the plane of the specimen, and hence have a folded conformation as before. In the study of polyethylene it was also observed[153] that increase in molecular mass is accompanied by a sharp increase in diamagnetic susceptibility in the region of transition from alkane crystals having straightened chains to polyethylene crystals with a folded conformation, reaching and even somewhat exceeding the values corresponding to liquid alkanes. It was then found that in the same region the diamagnetic susceptibility of molten polyethylene also increases, to a value typical of gaseous alkanes. Comparison of experimental data on the optical anisotropy of macromolecules, the root mean square distances between the ends of a chain, and several other similar characteristics of polyethylene with values calculated for models of chains containing straightened segments of various lengths showed[154] that most satisfactory agreement is obtained with lengths of 10–20 monomer units. Investigation of the dependence of the density and the surface tension of narrow polyoxyethylene fractions on molecular mass revealed a minimum in the range of values of this last factor (~ 3000) at which chain folding began on crystallisation. Similar types of relations were obtained with non-crystallising oligomers of diethylene glycol adipate[155,156].

In concluding this survey of experimental results of the application of structural methods to amorphous polymers we must also remark that the repeatedly noted ambiguity and sometimes even inconsistency of the direct structural information, the very wide range of highly specialised methods of investigation and the consequent great dispersion of literature sources among the pages of several dozen different periodicals, and several other similar factors led to the appearance of a number of models of the amorphous state arising from the need for a logical explanation of anomalies in the macroscopic properties of polymers—the molecular-domain model to describe rheological phenomena and mechanical breakdown[157], the folded-fibrillar model to explain anomalies in the recovery from forced elastic deformation[158], its cluster modification[159], the dislocation model for viscous flow[160], the associative model to explain dynamic mechanical data[161], etc. A distinguishing feature of such models is unnecessary detail, structural evidence for which is at present completely lacking.

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Several important characteristics of the structure of amorphous polymers have been reliably established by the broad application of the traditional and the most recent resources of physical experiment to its analysis.

Firstly mention must be made of determination of the dimensions of individual macromolecules in isotropic block specimens (root mean square distance between ends of chain and weight-average radius of gyration) from data on the small-angle scattering mainly of neutrons. The principal result of these investigations is that the size of macromolecules is proportional to the square root of their molecular mass, and exceeds the size of a Gaussian coil by ~ 20%.

The next important conclusion, based on the diffraction of X-rays and electrons at large scattering angles, is that segments of chains are folded roughly in parallel in microregions of dimensions 20–50 Å. The scattering of X-rays at small angles indicates further that the density of such microregions differs very little from that of portions with skew contacts between chain segments (by 1.5% or less).

Despite the slight differences in density, these inhomogeneities in the packing of macromolecules could be visualised by the correct application of various procedures in electron microscopy (contrast enhancement, etching, dark-field technique, phase contrast effects).

The hypothesis of chain folding in the formation of ordered microregions in amorphous polymers has gained great popularity. It is based on certain theoretical arguments and several experimental analogies with the phenomena of chain folding in single crystals of polymers. Nevertheless, it must be borne in mind that all experimental results relating to chain folding have been obtained for the amorphous state of crystallisable polymers.

Of the large number of schematic models of the structure of amorphous polymers in the unoriented state (on the scale up to ~ 100–200 Å) those of Vainshtein and of Yeh and Geil, which differ merely in whether folding of macromolecules is essential, correspond most completely to the above characteristics.

Structural data at present available for dimensions of the next scale (200–9000 Å) are few and contradictory. Reliable data on the structure of the oriented state of amorphous polymers are almost completely lacking, and it is here that important advances in our knowledge of the fine structure of amorphous polymers must be expected in the very near future.

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The Porous Structure of Polymers and the Mechanism of Sorption

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A survey is made of the behaviour of polymeric sorbents and the role of the porous structure of polymers in the mechanism of sorption and in the thermodynamic affinity of solvents for the polymer. The list of references contains 301 items.

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I. INTRODUCTION

The properties of polymeric materials depend not only on the chemical structure and the dimensions of the macromolecules but also on the structure of the material, by which is usually understood the relative arrangement of macromolecules in space, their conformations, and also the internal structure of the units forming the macroscopic polymeric material and the nature of the interrelationship between them[1,2]. Furthermore, the concept of structure must include also looseness or emptiness, which are present in any material owing to the distances both between molecules and between coarser, supermolecular structures. In crystal chemistry these voids are indicated quantitatively by the packing coefficient[3,4]; the term "free volume" is usually applied to liquids[5]; and for porous solids various parameters of the porous structure are calculated[6].

A vast literature, summarised in several monographs[1,7,8], has been devoted to the structure especially of crystalline polymeric materials. These publications do not pay due attention to problems of the looseness of molecular packing and the porous structure of polymers, but are concerned mainly with the degree of ordering of the macromolecules and various morphological formations. Yet many papers have paid special attention to problems of the density of packing and the porous structure of polymers, but the regularities reported in them have not hitherto been summarised. Without knowledge of the porous structure of polymers and the density of their molecular packing it is impossible to describe the polymer structure, in particular of amorphous polymers, to understand the mechanism of the sorption of simple substances on polymers, or in general to comprehend the mechanism of the interaction of polymers with solvents.

The problem of the mechanism of sorption on polymers is of immense practical importance in connection with the expanding application of polymers as sorbents (ion-exchange resins and their frameworks, sorbents for gel-permeation chromatography)[9-11] and membranes (in particular for reverse osmosis[12-14]), as well as in connection with the sorption of simple substances by fibres, artificial leather[15,16], etc. Sorption effects play a large part in the permeability of polymers to gases and vapours[17,18]. Many processes in which polymers undergo chemical modification (e.g. the acetylation of cellulose, etc.) depend on the size of the pores, which act as transport arteries for penetration of the modifying agents to the reaction centres[19]. In this case an insufficiently developed porous structure may result in a non-uniform fibre of low quality. The mechanical and thermophysical properties of polymers are governed by their porous structure and the density of packing of the macromolecules[20,21]. It is therefore necessary to have a clear idea of the laws of the formation of the porous structure of polymers, and on the other hand also those of the production of monolithic polymers. The Reviewers have now made the first attempt to summarise all the information that has been published on this subject.

II. POROUS STRUCTURE OF MATERIALS AND ITS ESTIMATION

The concept of "porosity" and "pore" arose from consideration of the structure of solid mineral sorbents and catalysts. According to Dubinin's definition "pores are voids in solids ..."[22]; "porosity is a property of solids due to their structure and apparent in the presence of empty spaces—pores between individual grains, layers, crystallites, and other units of the coarse structure of a solid"[23]. The two definitions emphasise that the concept of porosity is applicable to solids, and that a pore is a space not between molecules but between supermolecular structures.

Table 1.

Method	Pore sizes, cm
Sorption	$10^{-7}-10^{-5}$
Chromatographic	$10^{-7}-10^{-5}$
Mercury porometry	$10^{-7}-10^{-3}$
Electron microscopy	$10^{-6}-10^{-4}$
Optical microscopy	$> 10^{-4}$
X-Ray diffraction	$10^{-8}-10^{-5}$

The porosity of solvents is usually assessed quantitatively by means of several parameters—specific surface S_{sp}, total pore volume W_0, pore radius r—and by means of differential distribution curves of pore volume with respect to radius. Methods of determination developed for mineral sorbents[24-26] are applied also to polymers. Each method covers a definite range of pore sizes (Table 1).

The most direct visual method is electron microscopy, which makes it possible to assess not only the dimensions but also the shape of the pores[27-29]; it is applied also to polymers[30-42]. X-Ray diffraction enables the effective radii of the finest pores to be determined[43,44]; in recent years this method has been widely applied to investigate ultramicrocracks in polymers[21,45], which are essentially micropores.

The sorption method was historically the first for evaluating the porous structure of sorbents, and has become classic. It consists essentially in studying the sorption of various substances from liquid and vapour media on solids and then using the resulting sorption isotherms to calculate the specific surface, the total pore volume, the pore radius, and the differential distribution curves. There exist many variants of this method and ways of calculating the parameters of the porous structure. The most common are the Brunauer–Emmett–Teller (BET) method for calculating specific surface[46,47] and the Dubinin–Radushkevich equation for calculating the total pore volume[48]. Despite the widespread use of the sorption method, it has several limitations, as indicated below.

1. It cannot estimate voids having $r < 7$ Å, since the quantity of substance sorbed by them is below the limits of sensitivity of the method.

2. Values of W_0, calculated by means of the Dubinin–Radushekvich equation or directly from the maximum quantity of substance sorbed[49], do not represent the true total pore volume, but indicate essentially the limiting volume of adsorption space, which, of course, depends on the size of the sorbed molecules: the larger the molecules the less accessible are the fine pores of the sorbent and hence the smaller the value obtained for W_0. In order to estimate the dimensions of the finer pores, therefore, use must be made of the sorption of substances having small molecules (nitrogen or argon); this is performed at temperatures at which their vapours condense (low-temperature sorption). In most cases the "porosity for nitrogen" of mineral sorbents exceeds the "porosity for benzene".[50] However, some workers[51,52] refer to quite marked changes in pore volume accompanying the cooling of certain mineral sorbents to temperatures (around −200°C) at which the sorption of nitrogen or argon is conducted, which may lead to incorrect results.

3. The parameters of the porous structure depend on the chemical surface structure of the sorbent, which in turn affects the area, occurring in the BET equation, occupied by a sorbate molecule in the adsorption layer and the degree of wetting of the surface by the liquid, i.e. the process of capillary condensation. Poor surface wetting hinders this process and leads to underestimates of the parameters[53].

4. Calculations based on the Thomson–Kelvin equation do not give true pore radii but essentially the radii of concave menisei of liquid condensed in the pores. A correction for the thickness of the adsorption layer must be made to obtain true pore radii[54,55].

5. The sorption method does not enable the size of very large pores to be estimated, in which capillary condensation is difficult because of the considerable distance between the walls.

The porous structure of solids can be investigated over a wide range of pore sizes by the method of mercury porometry, which enables pore radii to be measured from 30 to some 10^5 Å:[26,56-58] the larger pores (10^4–10^5 Å) are filled with mercury under pressures of ~ 1 atm; high pressures reaching 2500–4000 atm are used to fill the finer pores. The pore radii are calculated by means of the equation

$$r = -\frac{2\sigma \cdot \cos\theta}{p}, \tag{1}$$

where σ is the surface tension of mercury at the experimental temperature, θ the angle of wetting, and p (in kgf cm^{-2}) the pressure. This method has recently begun to be widely used to examine the porous structure of polymeric materials—fibres[59-69], network copolymers, and ion-exchange resins based on them[34,70-75].

Difficulties arise also with mercury porometry, connected with the choice of numerical values for σ and θ, which depend on the nature and the purity of the surface, and may vary with pressure[26,60,76,77]. As a result of incorrect estimates for σ and θ, as well as their possible variation during an experiment, the error in the determination of pore size may reach 30–40%.[26,77] Furthermore, the high pressures applied may disrupt the structure of the sorbent[26,51,65,76-80]. Therefore this cannot be regarded as an absolute method for determining pore size[75,77].

III. CHARACTERISTICS OF POLYMERIC SORBENTS

All that has been stated above concerning the limitations on the sorption method and mercury porometry are fully applicable also to polymeric sorbents, which also possess specific features due to the properties and structure of the polymers. In the determination of the pore structure of polymers it must be borne in mind that they exist not only in the solid but also in the rubberlike-elastic state, so that the question naturally arises of whether the idea of pores and porosity is appropriate to such a state. From the definition of these concepts (Section II) it follows that pores are voids in a solid that do not change with time[81]. This concept is fully applicable to solid polymers (vitreous and crystalline) but inapplicable to polymers in a state of rubberlike elasticity. In this last case the "voids" or "holes" have a fluctuating character (just as in liquids): i.e. they change their forms and dimensions continuously under the influence of thermal motion. However, the permanent cavities produced in polymeric materials under special conditions, e.g. in foam rubbers, can be termed pores, and the articles themselves are porous.

Furthermore, the structure of polymeric sorbents is considerably more labile and far more sensitive to sorbent–sorbate interaction, temperature, and external pressure than is the structure of classic mineral sorbents (active carbons, silica gels, etc.). This faces the investigator with the problem of the conditions under which a particular method can be used to assess porous structure, and also the conditions of preparation of polymeric sorbents.

Any substance of high molecular weight swells on interaction with liquids and vapours of low molecular weight. Swelling is not simply the absorption of these substances by the pores of the former: it necessarily involves changes in the volume of the specimen and in its structure[82]. Hence the structure of a swollen polymer differs fundamentally, especially at high relative vapour pressures, from its original structure. Since a swollen polymer is not a solid, the "holes" or free volume it contains are fluctuating in character and are not pores. Therefore the terms used in the literature—"porosity of polymers in the hydrated state"[10], "pseudoporosity"[83], "latent porosity"[84-86]—are devoid of physical meaning.

Structural lability of a polymer develops also when the temperature is varied, which often leads to incorrect results in the investigation of the low-temperature sorption of nitrogen or argon vapour[87-94]. If the coefficient of thermal expansion of a sorbent is $\alpha \simeq 10^{-6}$ deg^{-1}, the specific volume may change by only 0.002–0.003 cm^3 g^{-1} when the temperature is lowered from 25 to −195°C, and this will hardly be apparent in its overall porosity. In such cases the porosity with respect to nitrogen, determined at −195°C, will exceed the porosity with respect to benzene, determined at 25°C, as was to be expected, and the method of low-temperature sorption is applicable. With many polymers, however, the coefficient of expansion is larger by factors of $10-10^2$. For example, polystyrene and its copolymers have $\alpha = (1.8-2.7) \times 10^{-4}$ deg^{-1}, and for cellulose $\alpha = 4 \times 10^{-4}$ deg^{-1};[93,94] hence the volume of these compounds should decrease by 0.1 cm^3 g^{-1} when they are cooled by ~ 200 deg. If the pore volume of the polymer is of the same order, the porosity will almost disappear on cooling. In such cases the parameters of the porous structure determined with respect to nitrogen may be smaller than those with respect to organic compounds. This is illustrated by Table 2, which shows that, for specimens of well developed porosity (No. 4 and 5), such volume changes are insignificant, and the specific surface with respect to nitrogen is considerably larger than that with respect to methanol[94]. It is obviously for this reason that results obtained by Ruzička and Kudlaček[95] for the sorption of argon vapour on viscose tyre cord agreed with those obtained by Paul and Bartsch[96] for high-strength viscose rayon fibre by mercury porometry. In the case of polymers having relatively undeveloped porosity, however, the low-temperature sorption of nitrogen or argon vapour must be applied with great caution[94].

Table 2. Parameters of the porous structure of polymers determined from the sorption of nitrogen and organic vapours[94].

No.	Polymer	S_{sp}, m^2 g^{-1}		W_0, cm^3 g^{-1}	
		N_2	CH_3OH	N_2	CH_3OH
1	Polystyrene	—	—	0.001	0.030
2	Copolymer of styrene + 4% *p*-dvb*	~0	5.1	~0	0.030
3	Copolymer of styrene + 20% *p*-dvb	~0	17.2	~0	0.070
4	Copolymer of styrene + 60% *p*-dvb**	278.4	88.4	—	0.460
5	Polymer based on 100% *p*-dvb**	423.8	94.2	—	0.440

* dvb = divinylbenzene.

** Synthesised in n-heptane.

The structural lability of polymers and polymeric sorbents is evident also in mercury-porometric measurements, since the high pressures used may develop forced elastic deformations in the specimen. In uniformly porous polymers, with all the pores filled with mercury at almost the same pressure, the pore walls may be compressed under multilateral pressure. When pores of different sizes are present, they are filled with mercury at different pressures, and the wall between a full pore and a still unfilled pore may be deformed by unilateral pressure, closing the pore. The possibility of the reversible compression of polymers during porometric measurements was mentioned in Ref. 65, but with some polymers no significant change in porosity occurs when they are tested in a porometer[75].

The peculiarities of polymeric sorbents also lead to certain demands on their preparation, mainly the need to remove from the pores various impurities of low molecular weight. With active carbons and other mineral sorbents this is usually achieved by prolonged heating in a vacuum at 300–400°C. Such heat-treatment is excluded with polymers because of their possible degradation or other chemical changes. But the removal of moisture or organic compounds by drying polymers even at lower temperatures (but above their glass points) is also hardly applicable because of shrinkage phenomena due to the plasticising action of low-molecular liquids that are present. Thus the vaporisation of water from moistened cellulose leads to its compaction[19].

Polymeric sorbents can be subjected to lyophilic or freeze drying, first applied to biological materials. This method consists in the rapid cooling of moistened polymer specimens to the boiling point of liquid nitrogen, which leads to the sublimation of liquids present in the specimen. An advantage of lyophilic drying is the almost complete elimination of the effect of the capillary forces present in ordinary drying[97-102].

The best method for drying a polymer is inclusion, which consists in successive displacement of the liquid by treatment with various increasingly volatile miscible liquids which possess gradually diminishing affinity for the polymer. The last liquid should have as low a surface tension as possible. As a result, the polymer passes into a vitreous state, and its pores contain a readily vaporisable liquid interacting only slightly with the polymer. After removal of this liquid the polymer has more or less retained its original structure[19,67,68,98,99,103-105]. The classic example of this method is the inclusion of moistened cellulose: water is displaced by repeated treatments with methanol, and then with pentane, which is evaporated off[19].

Unfortunately, these characteristics of polymeric sorbents were ignored in many determinations of the porosity parameters, so that the results are unreliable[87,89,106,107]. For example, the specific surface of cellulose was calculated from the water-vapour sorption isotherms as 100–200 m^2 g^{-1},[87,106] values which are far too high, since cellulose swells strongly in water. If the sorbates used cause a given polymer to swell to different extents, different values of the specific surface will, of course, be obtained for the same specimen[107].

The incorrectness of such results was first pointed out by the Reviewers[108,109], who suggested the same approach as for mineral sorbents, i.e. to maintain the sorbent as far as possible rigid, retaining its structure unchanged during sorption. The appropriate sorbates were said to be "inert", a not altogether fortunate term, since absolutely inert sorbates and sorbents do not exist, as Hill showed[110-112]. Any sorbent—even if mineral—undergoes some perturbation under the influence of a sorbate, which is apparent in a change in state of the surface atoms[113-115] or even in a slight "subswelling" of the sorbent[116-119]. Henceforward, however, we shall employ the term "inert" to imply sorbates in which a polymer hardly swells at all.

Polymeric sorbents may undergo considerable disturbances under the influence of a sorbate. In order to obtain correct values for the parameters of their porous structure it is necessary to select for each polymer a sorbate that will not cause its bulk swelling (the perturbation of a polymeric sorbent by the sorbate should not exceed that of a mineral sorbent).

During recent years comprehensive experimental information has been obtained on the sorption of "inert" vapours (i.e. those that do not cause swelling) on very many polymers[49,93,94,108,109,120-141]. Parameters of their porous structure have been calculated (by generally accepted methods) from the sorption isotherms. The BET and Dubinin–Radushkevich equations are applicable over the same ranges of relative vapour pressures as for mineral sorbents[108,120,130].

IV. CLASSIFICATION OF POLYMERIC SORBENTS AND THE POROUS STRUCTURE OF POLYMERS

The first few classifications of mineral and polymeric sorbents were based on the form of sorption isotherm, which was related to the type of surface coverage of the adsorbents by the adsorbate molecules. In particular, such a classification was proposed by Brunauer, Deming, Deming, and Teller (the BDDT classification), in which all published sorption isotherms were divided into five types differing in the character of the surface coverage[6,24]. A similar approach to the classification of polymeric sorbents was suggested by Rogers, who separated all known sorption isotherms on polymers into the four types[142] illustrated in Fig. 1. The first type of isotherms correspond to a linear relation between the concentration of the sorbed substance and the pressure, which characterises the absorption of a gas in conformity with Henry's law. The second type involve systems in which only a monolayer is adsorbed on the polymer surface. Isotherms of the third type are obtained for multimolecular adsorption when the energy of interaction between sorbent and sorbate molecules exceeds the intermolecular interaction energy in the sorbate. The fourth type corresponds to multimolecular adsorption when the former interaction energy is very much smaller.

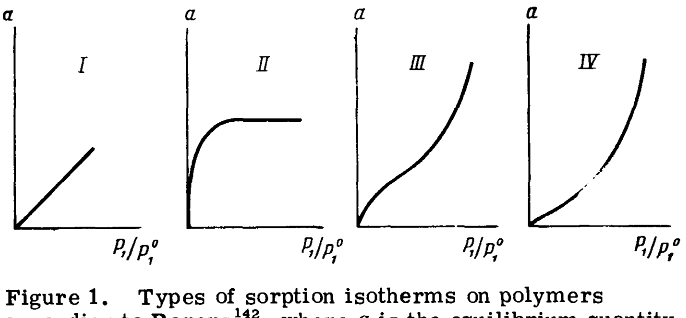

Figure 1. Types of sorption isotherms on polymers according to Rogers[142], where a is the equilibrium quantity sorbed in millimoles per gram of sorbent, and p_1/p_1^0 the relative vapour pressure.

Theories relating adsorption processes solely with surface state[24] were accompanied by the development of ideas on the role of sorbent porosity in adsorption processes, and classification of mineral sorbents were proposed according to pore size and shape. Thus there exist globular, slitlike, cylindrical, and bottle-shaped pores, as well as pores between round rods[116]. Pores are divided into closed, blind, and open pores[51,143]: the third group comprises pores, channels, and capillaries that are connected with one another and with the sorbent surface, serving as transport arteries for mass transfer; closed pores are mutually isolated and have no outlet to the surface; and blind pores are connected with the surface but are not interconnected. No unambiguous evidence has been published of the presence of one kind of pore or another. In most cases this must be judged from gas-permeability data[144,145]. The most fertile classifications of sorbents are those of Dubinin[6,22,146] and of Kiselev[147], which can be applied even to polymeric sorbents.

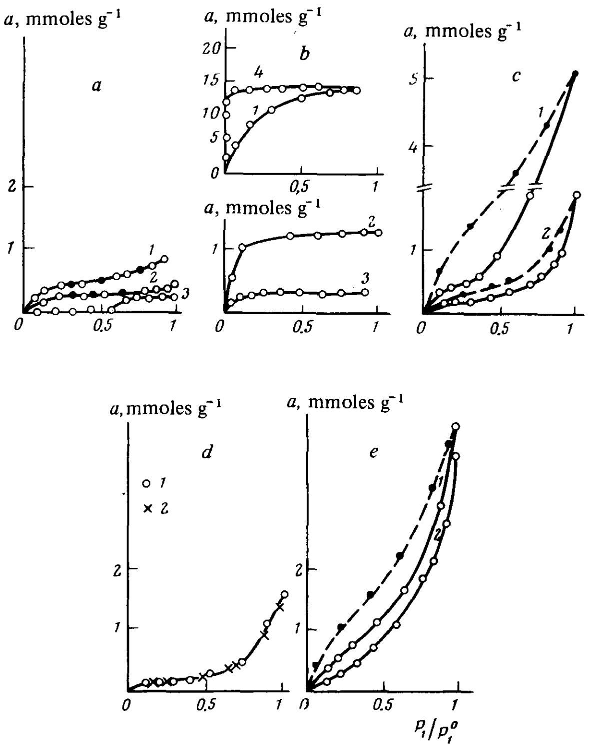

Figure 2. Sorption isotherms for vapours of "inert" liquids on different classes of polymeric sorbents, where the solid circles and broken curves denote desorption results. (*a*) Non-porous: 1) n-hexane on polyvinyl alcohol[108]; 2) benzene on polyvinylidene chloride[121]; 3) methanol on polyethylene[121]. (*b*) Microporous: 1) nitrogen on a macroscopically cross-linked isoporous polymeric sorbent based on polystyrene and *p*-bischloromethylbenzene; 2) water on polystyrene[148]; 3) n-hexane on cellulose[108]; 4) nitrogen on activated carbon[123]. (*c*) Sorbents containing continuous pores: 1) copolymer of styrene with *p*-divinylbenzene (in n-decane)[131]; 2) methanol on a polyarylate (DKh-1 brand)[237]. (*d*) Macroporous: 1) Styroflex film; 2) polystyrene film. (*e*) Mixed type: 1) copolymer of styrene with technical divinylbenzene (in n-heptane)[125]; methanol on a polyarylate (F-1 brand)[237].

Analysis of > 200 sorption isotherms for "inert" vapours on various polymers[49,93,108,109,120-141,148] enables them to be separated into the four main types illustrated in Fig. 2. The first type—non-porous sorbents (Fig. 2*a*)—are characterised by sigmoid isotherms without sorption hysteresis and with a small quantity of maximally absorbed sorbate. Such isotherms are observed with several crystalline polymers (polyvinyl alcohol, polyvinylidene chloride) and certain densely packed vitreous polymers (block poly(methyl methacrylate) and polystyrene). At low relative vapour pressures crystalline polyethylene sorbs hardly any vapour of the "inert" methanol, and insignificant sorption is observed only at higher relative vapour pressures. Such polymers are characterised by almost zero total pore volume W_0 and very small specific surfaces (~ 1–7 m^2 g^{-1}).

The second type comprises microporous polymeric sorbents having pore radii up to 16 Å. Such fine pores cannot be penetrated by large sorbate molecules and many small molecules. Microporous sorbents are characterised by Γ-shaped isotherms (Fig. 2*b*), the plateau on which results not from surface saturation with sorbate molecules but from the inaccessibility of the fine pores to the penetration of many molecules. The concept of specific surface has no physical meaning for microporous polymeric sorbents[22,149-154], but the total pore volume may reach 0.5 cm^3 g^{-1}. Fig. 2*b* indicates that the initial portion of the sorption isotherms is considerably less steep on the polymeric sorbents than e.g. on microporous carbons[123,155] or zeolites[156-159]. This is understandable, since a large number of fine pores in the latter sorbents result from the removal of hydrogen chloride or water.

Polymeric sorbents of the third type have continuous pores with radii from 16 to 1000–2000 Å. Such polymers are characterised by sigmoid isotherms and large sorption hysteresis (Fig. 2*c*). They are able to absorb large quantities of a sorbate, their total pore volume reaching $W_0 \simeq 0.8$ cm^3 g^{-1} and their specific surface ~ 700–900 m^2 g^{-1}.

Macroporous polymeric sorbents, having pore radii exceeding 1000–2000 Å, constitute the fourth type. According to Dubinin's hypothesis, sorption takes place on them in the same way as on non-porous sorbents, since the internal surface of such large cavities acts as an external surface. Indeed, Fig. 2*d* shows that the sorption isotherms for methanol on a non-porous Styroflex film and on a specially prepared macroporous specimen of polystyrene are completely identical.

It is often impossible to assign real polymers to a definite class of sorbents, and in particular it is a complicated task to obtain uniformly fine-pored sorbents, often termed "isoporous". The latter are obtained not by polymerisation or polycondensation but by the cross-linking of existing polymers[136,160-163]. The large majority of amorphous polymers are sorbents of structurally mixed type. They are characterised by slightly sigmoid isotherms (Fig. 2*e*) and possess pores of the most diverse dimensions, as is evident from Fig. 3. Such sorbents often exhibit no correlation between pore volume and specific surface. Thus, when large pores predominate, the pore volume may be large but the specific surface small; and conversely, in the presence of a large number of small pores, the sorbent has a large specific surface and a small pore volume[49,129,135].

Pore radii of the order of 10^2–10^4 Å indicate that the large cavities in the polymer are formed not between molecules but between coarse supermolecular structures, while the pore walls may be very densely packed. This suggests that amorphous polymers are structurally inhomogeneous, as is sometimes observed even with crystalline polymers. In isotactic polystyrene, for example, large pores are found situated between crystallites[122].

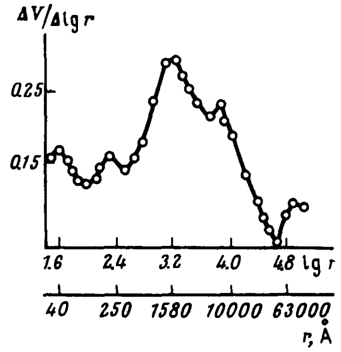

Figure 3. Differential curve of the distribution of pore volume with respect to radius for F-1 polyarylate, where ΔV is the volume of mercury filling pores of certain radii.

Porosity is not a property of a given substance but depends on its previous history. It is usually produced during preparation of the specimen. Several methods are available for obtaining porous polymers, and are used during synthesis and the moulding of articles. They usually involve heat-treatment of the material accompanied by removal of volatile products[123,161-170], with the introduction of special blowing agents[10,171], saturation of the polymers by gases under a high pressure which is subsequently released[172], or the introduction into monomers of suspensions of organic or inorganic solids which are later removed[173,174]. One process for obtaining porous polymers is synthesis in the presence of a solvent, whose removal leaves quite large cavities in the polymer. Very porous three-dimensional polymers can be synthesised in so called inert solvents, i.e. substances that are not involved in the polymerisation. Porous cross-linked copolymers (e.g. of styrene with divinylbenzene), employed in chromatography and also used as frameworks for macroporous ion-exchange resins, are produced in this way[9,10,31,32,83-86,136,174-180]. Shrinkage stresses arising on removal of the solvent then play an important part. They lead to shrinkage deformations and to contraction of the structural framework, i.e. to shrinkage of the whole material.

This phenomenon was investigated in detail by Rebinder[181], Ostrikov et al.[182-190], Vlodavets et al.[191-193], etc. The shrinkage stresses may result in contraction of the material by factors of 8–10[194], with the pore walls coming together and in some cases completely closing the pores[181,185,191]. The magnitude of the shrinkage stresses depends on the surface tension of the liquid[67,98,103-105,185,194-198], the nature of the sorbent, and the shrinkage capacity of the latter[199]. With perfectly rigid materials (porous silicate glasses, ceramics) shrinkage phenomena are almost completely absent. Elastic polymers exhibit the largest shrinkage. Hence the polymer framework should be as inelastic as possible to obtain a highly porous structure during removal of the inert solvent, as has been demonstrated experimentally for the cross-linked frameworks of styrene–divinylbenzene copolymers[200]. This is achieved by introducing a large number of cross-links during synthesis and selecting as inert solvent a "poor" solvent that does not plasticise the polymers. Cross-linked copolymers of highly developed porosity are therefore obtained in the presence of large quantities of thermodynamically "bad" solvents and with a large quantity of the cross-linking agent in the reaction mixture[31,32,34,49,70–72,84–86,124,125,131,136,173,174,176,180,201–224].

Analogous effects are observed also in the synthesis of linear polymers, as has been shown for a series of polyarylates[133,135]. Thus polymers of desired porosity can be obtained by varying the conditions of the synthesis. A porous structure can be conferred on polymers also by varying the conditions under which they are moulded, as has been demonstrated for fibres[64,67,68,225–228] and films[129,132,229–237].

V. RELATIONS BETWEEN PARAMETERS OF THE POROUS STRUCTURE OF POLYMERS, THEIR FREE VOLUME, AND THE PACKING COEFFICIENT

As already mentioned, besides the term "porosity" there exist other concepts connected with "empty" spaces in materials—the free volume and the packing coefficient—the problem of whose relationship has been discussed previously[238].

The term "packing coefficient" was first applied by Kitaigorodskii to crystals[3,4], but subsequently began to be used for amorphous solids and liquids, and also to describe the molecular packing of polymers[239–243]. This coefficient is the ratio of the actual volume of the molecules in 1 g or 1 mole of the substance to its specific (or molar) volume at the given temperature:

$$K = \frac{V_W}{V_T}. \tag{2}$$

The intrinsic volume of molecules is calculated from the intermolecular distances and the lengths of the chemical bonds between the atoms, obtained by X-ray diffraction[4,240]. For most low-molecular and polymeric crystals the packing coefficient lies in the range $K = 0.68–0.8$,[3] and for monolithic amorphous polymers it fluctuates between 0.662 and 0.723.[240]

The free volume is usually understood to be the volume not occupied by the mass of the given substance, but different authors calculated it differently. Thus Frenkel'[5] understood by free volume the excess volume of a specimen at a given temperature in comparison with its volume at the absolute zero:

$$V_F = V_T - V_0. \tag{3}$$

Hildebrand and Bondi termed the quantity V_F calculated by means of Eqn. (3) the expansion volume, and proposed that the free or empty volume V_E should be calculated by means of the formula[244,245]

$$V_E = V_T - V_W, \tag{4}$$

in which V_T is the volume of the body at the given temperature and V_W is the actual volume of its molecules.

The empty volume and the packing coefficient are related by the simple formula

$$1 - K = V_E/V_T, \tag{5}$$

from which it follows that in crystals, even with the densest packing of their atoms and molecules, the free or empty volume constitutes 20–32% of the total volume. Yet sorption experiments show that typical crystalline solids are non-porous sorbents. Hence 20–32% of the volume of crystalline solids represents "ultramicroscopic voids" inaccessible to even the smallest gas molecules, e.g. hydrogen[246]. Diffusion in the lattice of such crystals as sodium chloride, etc. is possible only when they contain defects or at high temperatures[246].

As already mentioned, crystalline polymers are in most cases also non-porous solvents, for which calculations show that V_E fluctuates within the range 0.2–0.3 cm^3 g^{-1}.[237,238] If Eqn. (4) is formally used to calculate V_E for a porous polymer, the very high values of 2–4 cm^3 g^{-1} are obtained. This empty volume obviously includes the whole total pore volume. Thus the free or empty volume of a porous polymer always exceeds its total pore volume. However, the quantity W_0 calculated from sorption data does not represent the total pore volume, since it depends on the relation between the size of the pores and that of the sorbate molecules (Section II). This led to introduction of the concept of the maximum pore volume $W_0^{\max}$, representing the volume of all the pores into which molecules of any size can penetrate[238].

A hypothetical case can be imagined in which a polymer contains pores of various sizes, while the pore walls are packed as in an ideal crystal, so that

$$W_0^{\max} = V_T - V_{\text{id.cr}} \,. \tag{6}$$

This recalls an equation often used to calculate the total porosity[25,98,105] or the so called porosity factor[31]

$$P = 1/\rho_{\text{app}} - 1/\rho_{\text{tr}}, \tag{7}$$

in which ρ_{app} and ρ_{tr} are the apparent and true densities of the material respectively[31]. The former density is determined pyknometrically with a liquid that does not wet the material and hence does not penetrate its pores (most often mercury), or is calculated from geometrical considerations[25,247]. The true density is also determined pyknometrically but with a liquid that wets the polymer and hence is able to penetrate its pores. For non-porous materials $\rho_{\text{app}} = \rho_{\text{tr}}$. For porous materials, even if microporous, these quantities may differ markedly. Therefore the method used to determine the density of a polymer must always be indicated.

Table 3 lists some typical values for the parameters V_E and $W_0^{\max}$ and for the packing coefficients. It includes apparent polymer densities, which for polyisobutylene, polyethylene, and poly(vinyl acetate) are identical with the true densities. For the first four polymers in Table 3 we see that $W_0^{\max} \simeq 0$, so that the empty volume V_E is the volume of ultramicroscopic cavities, which fluctuates from 0.26 to 0.35 cm^3 g^{-1}. However, these polymers differ in their density of packing, which is especially clearly shown in the values of V_E expressed in cm^3 mole^{-1} monomer unit: its value is least for crystalline polyethylene, which has the highest packing coefficient. A less densely packed polymer is polyisobutylene, for which $K = 0.678$; it is followed by polystyrene and poly(vinyl acetate). These data show that polystyrene is a loosely packed polymer, as follows also from heats of dissolution[248,249]. It is interesting that these last two polymers have almost the same packing coefficients, and the values for all amorphous polymers are very closely similar[240]. The empty volume V_E calculated in cm^3 mole^{-1} is probably a more sensitive measure of density of packing.

Polyarylates possess very high values of W_0^{max}, V_E (cm^3 g^{-1}), and V_E (cm^3 mole^{-1}). The porosity of these polymers is a consequence of their synthesis in solvents. Values of K calculated formally by means of Eqn. (2) for such polymers are far smaller than for non-porous polymers. Such low packing coefficients indicate not a low density of molecular packing but a loose packing of supermolecular structures. Consequently porosity and density of molecular packing are inadequate concepts.

Table 3. Densities, free volumes, maximum pore volumes, and packing coefficients of polymers[237,238,240].

No.	Polymer	ρ_{app}, g cm^{-3}	V_E, cm^3 g^{-1}	V_E, cm^3 mole^{-1}	W_0^{max}, cm^3 g^{-1}	K_{pol}
1	Polyethylene (100% cryst.)	1.00	0.26	7.2	~0	0.740
2	Poly(vinyl acetate)	1.189	0.28	24.1	~0	0.665
3	Polystyrene	1.05	0.32	33.3	0.06	0.666
4	Polyisobutylene	0.912	0.35	10.6	0	0.678
5	Polyarylate based on phenolphthalein and isophthalic acid—F-1 (synthesised in chlorinated biphenyl)	0.90	0.82	367.3	0.58	0.477
6	Polyarylate based on phenolphthalein and terephthalic acid—F-2 (in acetone)	0.77	0.74	355	0.49	0.426

VI. MECHANISM OF THE SORPTION OF SIMPLE SUBSTANCES BY POLYMERS

The absorption of one substance by another, e.g. of a liquid by another or of gases by liquids, is in general termed sorption. More often, however, this term implies the absorption of molecules of gases, vapours, or liquids or of ions by solids, which can occur by two mechanisms[24]. (1) The substance is absorbed only on the surface, whether external or internal. Such a process is termed adsorption. It is divided into physical adsorption, when the adsorbate interacts with the adsorbent by van der Waals forces, and chemisorption, when chemical reactions occur between them. (2) Molecules of the sorbate penetrate inside the solid, entering the force field existing between its atoms, ions, or molecules throughout. Here, too, two processes may occur: the gas or vapour can either dissolve in the solid or form a chemical compound with it. For the most part adsorption and dissolution occur simultaneously, and are combined under the general term sorption.

The mechanism of the sorption of low-molecular substances on polymers is complicated and depends on many factors, including the phase constitution and the physical state of the polymer, its porous structure, its chemical structure, the flexibility of the chains, intermolecular interaction, and the thermodynamic affinity of the polymer for the sorbate. Depending on the magnitude of this last factor the polymer may be perturbed to different extents and the mechanism of sorption may be different.

1. Mechanism of the Sorption of "Inert" Sorbates on Polymers

If the polymer does not swell in the sorbate vapour, the mechanism of sorption does not differ fundamentally from that on mineral sorbents. Thus physical adsorption takes place on non-porous crystalline or elastic polymers (we ignore chemical interaction between polymer and sorbate).

Interacting centres of a microporous sorbent are distributed throughout its volume. With such sorbents, therefore, a mechanism of bulk filling of pores can be regarded as "dissolution" of the gas or "inert" vapour in the bulk of the specimen[22,154,250-252]. The mechanism operating with sorbents containing continuous pores involves coverage of the pore walls layer by layer, coalescence of the multilayers, and capillary condensation. Coalescence does not take place in macroporous sorbents owing to the distance between the pore walls, so that capillary condensation is absent, and only physical adsorption is observed.

Information on the mechanism of adsorption will be given by heats of adsorption, which has been discussed in detail by Kiselev et al. for hydrocarbons on graphitised carbon black, a typical non-porous adsorbent[253-256]. They showed that at low surface coverage the hydrocarbon molecules are oriented parallel to the surface. A similar conclusion has been reached by Ostrovskii et al.[257,258] in an investigation of the heats of adsorption of hydrocarbons on poly-p-divinylbenzene. This work showed that the BET theory of multimolecular adsorption does not apply to polymeric sorbents, which was attributed to surface non-uniformity. Analysis of possible reasons for such inhomogeneity indicated that the inconsistency with the BET theory might be due to swelling of the polymer, which will be considered in greater detail in the following subsection.

2. Mechanism of the Sorption of Non-inert Vapours on Polymers

Any substances in which polymers swell will be regarded as non-inert liquids and their vapours. Sorption of the vapours is most typical in the case of polymers. Numerous papers have appeared on the sorption of the most diverse vapours on various polymers—Long[259-267], Park[268-270], Gregor[271,272], Kargin et al.,[273-281] Tager et al.,[282-288] Lipatov et al.,[289] Papkov and Fainberg[15], and others. Inspection of the immense amount of information existing on the sorption of various substances on different polymers enables certain generalisations to be made and several mechanisms of sorption of non-inert substances typical of polymers to be distinguished. Thus with dense packing of macromolecules porosity is absent and physical adsorption is impossible. The sorption of non-inert vapours on densely packed polymers (elastic or vitreous, linear and cross-linked) must be regarded as true dissolution of the vapour in the polymer "matrix". However, dissolution has different mechanisms according as the temperature is above or below the glass point.

The mechanism of the dissolution of vapours in the elastomeric polymers (above the glass point) is fluctuational: i.e. the process consists in sorbate molecules and monomer units or segments of the polymer chain changing places. Because of the great flexibility of the chain these interchanges are possible from the very first portions of gas or vapour absorbed: i.e. disturbance of the sorbent and essentially mutual dissolution of the components begin at the lowest values of p_1. Typical sorption isotherms on elastic polymers are always concave [? convex] to the abscissae axis throughout the range of relative vapour pressures (Fig. 4a). The worse is the solvent thermodynamically, the lower is the sorption isotherm situated, and a non-solvent remains almost unabsorbed by the elastomers. The overall process depends on the affinity of the solvent for the polymer and on the flexibility of the polymer chain. With the same flexibility the sorption of a given substance on different elastomers is described by a single curve[277].

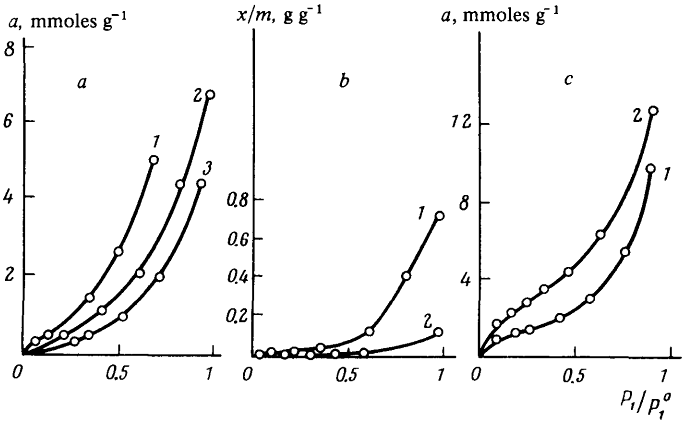

Figure 4. Types of sorption isotherms for vapours of non-inert liquids on polymers, where x/m is the equilibrium quantity sorbed expressed in grams: (*a*) 1) n-hexane on natural rubber[276]; 2) toluene on polyisobutylene[284]; 3) benzene on nitrile rubber (SKN-18)[282]; (*b*) 1) dioxan on polyurethane[287]; 2) ethanol on polyvinyl alcohol[276]; (*c*) 1) benzene on porous polystyrene[288]; chloroform on a polyarylate[237].

At temperatures below the glass point segmental motion of the chain is almost completely absent, so that interchanges between vapour molecules and chain units are difficult. The mechanism of dissolution of the vapour consists in the penetration of its molecules into existing cavities, of which there are few in densely packed polymers. The process is facilitated by the mobility of side-groups, but this effect is apparently insignificant, since at low pressures p_1 the quantity of substance dissolved lies beyond the sensitivity of the sorption method. Sorption begins to be appreciable at definite values of p_1, at which a fluctuational mechanism of swelling and dissolution of the polymer becomes possible. The sorption isotherms therefore have the form illustrated in Fig. 4*b* [278,287].

A more complicated mechanism of sorption of non-inert vapours is observed with porous vitreous polymers. The sorption isotherms are sigmoid with an initial section convex towards the ordinate (Fig. 4*c*). This portion corresponds to the vitreous state of the system[288]; the point of inflexion on the curve lies in the range of sorbate concentrations in the polymer at which the system passes, at the experimental temperature (25°C), from the vitreous state into one of rubberlike elasticity.

At higher relative vapour pressures the shape of the isotherm resembles that for elastomers: i.e. the mechanism of the absorption of a vapour by a polymer is analogous to the mechanism of sorption on rubberlike polymers. Sorption isotherms of this type have been obtained with cross-linked copolymers[271,272], polyamides[276], cellulose nitrate and acetate[290], and polystyrene[291]. Analysis of such sigmoid isotherms led to the conclusion[106,112,276,291,292] that the initial convex portion of the isotherm represents physical adsorption, and the concave portion corresponds to dissolution of the polymer, the main argument being that the former obeys the BET equation, and the latter the Flory equation.

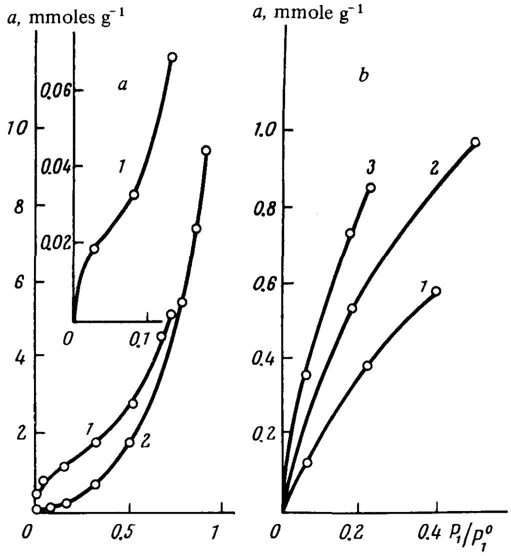

Figure 5. Sorption isotherms for the vapours of different liquids on specimens of polystyrene[288]. (*a*) Benzene vapour on polystyrene: 1) porous; 2) non-porous. (*b*) Initial portions of sorption isotherms on porous polystyrene for the vapours of: 1) methanol; 2) cyclohexane; 3) benzene.

A recent study of the sorption of various vapours on polymeric sorbents of the same chemical nature but differing in porosity has shown[288] that the height of the convex upwards section is greater the greater the porosity of the polymer, and for the same porosity the greater the thermodynamic affinity of the sorbate for the polymer (Fig. 5). This indicates the simultaneous occurrence of the processes—physical adsorption of the sorbate in the pores of the polymer and swelling of the rest of the polymer, i.e. of the pore "walls" or the polymer "matrix"—which cannot be separated. However, their simultaneous occurrence leads to very important conclusions.

Firstly, the specific surface of the polymer itself cannot be calculated when sorbates in which the polymer swells are used: i.e. the BET equation is not applicable to such a case.

Secondly, since physical adsorption is superimposed on swelling, the parameters of the thermodynamic affinity of the solvent for the polymer calculated from the sorption isotherms should depend on the porous structure of the polymer. In fact, different values of the chemical-potential difference for the solvent calculated by means of the equation

$$\Delta\mu_1 = RT \ln p_1/p_1^0, \qquad (8)$$

should be obtained for the same degree of absorption of the sorbate. When the corresponding difference $\Delta\mu_2$ for the polymer is calculated by means of the Gibbs–Duhem equation, different values are also obtained for specimens differing in porosity.

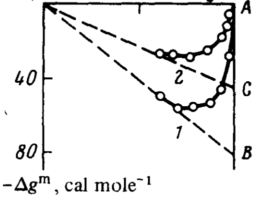

Figure 6. Dependence of Δg^m on apparent mole fraction x_2^* of the polymer (x_1^* is the apparent mole fraction of the solvent) for cyclohexane on polystyrene[288]: 1) porous; 2) non-porous.

Fig. 6 illustrates the mean free energies of mixing calculated by means of the formula

$$\Delta g^m = x_1^*\Delta\mu_1 + x_2^*\Delta\mu_2$$

as a function of the apparent mole fractions of the components. It is evident that they also depend on the porosity of the polymer. The difference between the free energies of interaction of the sorbate with porous and non-porous polymers is obviously the work required to form the pores, which can be calculated from the equations[288]

1 mole of units of non-porous polymer + solvent = soln. I - ΔG_{np}
1 mole of units of porous polymer + solvent = soln. II - ΔG_{por} ,

where ΔG_{por} and ΔG_{np} are the respective free energies of mixing of a large quantity of solvent with 1 mole of monomer units. Hence

non-porous polymer → porous polymer + $\Delta G_{por} - \Delta G_{np}$.

The difference $\Delta G_{por} - \Delta G_{np}$ represents the change in free energy accompanying transfer from the non-porous to the porous sorbent: i.e. it is the work of pore formation A_{por}. Values of ΔG_{por} and ΔG_{np} can be calculated from the dependence of Δg^m on x_2^*.[293] In Fig. 6 the intercept $AB = \Delta G_{por}$ (in calories per mole of monomer units in the polymer), while $AC = \Delta G_{np}$. The difference between them is the work of pore formation:

$$BC = AB - AC = \Delta G_{por} - \Delta G_{np} = A_{por} .$$

Values of A_{por} are independent of the nature of the sorbate, but increase with the porosity of the specimen[288].

The porous structure of a polymer influences also the magnitude and sign of the parameter χ_1 calculated by means of the Flory–Huggins equation[294]

$$\ln p_1/p_1^0 = \ln(1-\varphi_2) + \varphi_2 + \chi_1\varphi_2^2, \tag{9}$$

in which φ_2 is the volume fraction of the polymer. The concentration dependence of χ_1 is different for porous and non-porous specimens of a polymer (Fig. 7). For the latter the parameter increases with polymer concentration[294,295]. For a porous polymer χ_1 is a decreasing function of concentration at small dilutions, and the concentration dependence reaches negative values (curve *2*). Similar curves have been observed by Moore[290] for solutions of cellulose ethers, probably as a consequence of the sigmoid isotherms and the loose packing of these polymers. The above results indicate that Eqn. (9) holds only for the second stage of sorption, when the porous structure of the polymer has broken down and only swelling develops. If adsorption on the surface and sorption in the mass (swelling) take place simultaneously, the Flory–Huggins equation (9) cannot be applied.

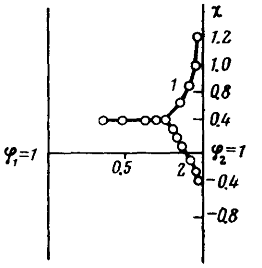

Figure 7. Concentration dependence of χ_1 (where φ_1 and φ_2 are the volume fractions of solvent and polymer respectively) for benzene on polystyrene[288]: 1) non-porous; 2) porous.

3. Role of the Porous Structure of Polymers in Sorption from Liquid Media and Vapours

An interesting phenomenon observed in the study of sorption processes is the Schroeder effect[296], according to which the quantity of a given substance absorbed by a polymer from a liquid medium always exceeds the quantity absorbed from the vapour state. It was first observed for the gelatin–water system. Analogous results were later obtained by other investigators[297–299] for the systems formed by agar-agar with water, unvulcanised and vulcanised rubber with organic liquids (alcohols, tetrachloromethane) and their vapours, and also liquid mixtures of benzene with alcohol and the mixed vapours sorbed on vulcanised rubber. The nature of the effect still remains an open question[299]. Schroeder himself[296] and the other investigators[297–299] attributed it to experimental error—fluctuations of temperature, the impossibility of achieving absolute saturation of the vapour, disregard of surface tension, a slower rate of sorption from liquid and vapour media, etc.

A more recent paper[300] has suggested, in addition to the above reasons, that the phenomenon may be due also to the presence of pores, which are filled with a liquid but not with a vapour. This hypothesis has been tested experimentally on several porous and non-porous polymers with both inert and non-inert liquids and their vapours[301]. It was found that with non-inert liquids, when the polymer swells, the Schroeder effect is not observed: i.e. the same equilibrium quantity of a substance is sorbed from liquid and vapour media. A difference is present only in the kinetics: liquids are sorbed more rapidly than are vapours (Fig. 8*a*, *b*). In the sorption of "inert" substances on porous polymers differences are observed not only in the kinetics but also in the equilibrium quantities sorbed (Fig. 8*c*): liquids are sorbed in far greater quantities than are their vapours.

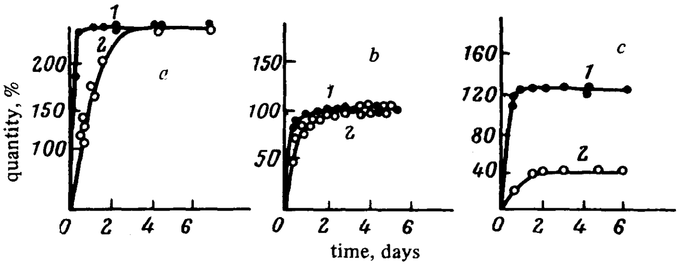

Figure 8. Rate curves for absorption by polymers from: 1) liquids; 2) vapours[301]: *a*) "non-inert" benzene on non-porous copolymer of styrene with 6% of divinylbenzene; *b*) "non-inert" benzene on macroporous copolymer of styrene with 20% of divinylbenzene; *c*) "inert" methanol on macroporous copolymer of styrene with 20% of divinylbenzene.

This last phenomenon is attributed to different mechanisms by which pores are filled. A liquid fills all the pores, including large pores, whose dimensions make them accessible to its molecules. But a vapour is sorbed by a more complicated mechanism, involving a series of successive stages—adsorption from the vapour on the pore walls with formation of multimolecular layers, coalescence of the latter with appearance of a concave meniscus, and then condensation of the vapour. Since the vapour pressure is lower the smaller the radius of curvature of a concave surface, capillary condensation occurs preferentially in fine pores (of continuous type). In coarse pores, as remarked in Section VI, 1, coalescence of multilayers and hence capillary condensation do not occur owing to the distance between the pore walls. Such pores may therefore remain unfilled by the "liquefied" vapour.

Thus development of the Schroeder effect depends both on the porous structure of the polymer and on the thermodynamic affinity of the low-molecular substance for the polymer. The absorption of substances that cause swelling involves a redistribution and partial disappearance of pores. Therefore the equilibrium quantity sorbed does not depend on whether it has been sorbed from the liquid or from the vapour.

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Thermodynamic Properties of Alkaline Earth Titanates, Zirconates, and Hafnates

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We shall review the problems arising during the critical analysis (aimed at selecting recommended values) of the thermodynamic constants of the alkaline-earth titanates, zirconates, and hafnates—a very important class of ferroelectric perovskites, widely used in radio electronics. Recommended values of the following standard thermodynamic quantities are given, with a statement of the uncertainty limits: the specific heat $C_{p,298}$, the enthalpy change $H_{298}-H_0$, the entropy S_{298}, the heat of formation $\Delta H_{f,298}$, the free energy of formation $\Delta G_{f,298}$, and the temperature and heat of phase transformation. The effect of impurities on the thermal constants of the phase transformations is discussed. The relationship between the thermodynamic characteristics and the crystal structure of perovskites is considered, with special reference to the effect of orthorhombic distortion of the ideal lattice on the entropy of the perovskite. In addition to thermodynamic methods we shall consider also other physical methods used to identify phase transformation temperatures, Curie points, and the temperature of the transition from the ferroelectric to the paraelectric state. Physical methods are especially important when the energy changes associated with the phase transformations are very small and cannot be detected by measurements of specific heat. 289 references.

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I. INTRODUCTION

Most of the thermodynamic data for rare-earth titanates, zirconates, and hafnates were obtained during the past 20 or 30 years. In this review we shall critically discuss the data published up to 1976 and we shall make a systematic choice of recommended values of the thermodynmic characteristics of these compounds.

In every case the standard entropy and enthalpy at 298.15 K was recalculated from the experimental data by the method described in Refs. 1 and 2. In these calculations independent interpolations of the specific heat were made at 5 K intervals for the range 5–100 K and at 10 K intervals for the range 100–300 K. Particular attention was paid to the relationship between thermodynamic characteristics and crystal structure. Most of the recommended data are compared with the most recent tabulations[3,4].

We have established a relationship between the thermodynamic formation quantities of the perovskites and the changes in the oxygen co-ordination polyhedron surrounding the cations. We have calculated the energy of the alkaline-earth cations Ca, Sr, Ba in the perovskite oxygen icosahedron, and also the energy of the transition of the zirconium and hafnium ions to an octahedral co-ordination of oxygen ions from the thermodynamically stable modifications of ZrO_2 and HfO_2. We have shown that the heat of formation of the perovskites from the simple oxides is directly proportional to the sum of the energies of the cation transitions involved in the formation of the perovskite structure. We have established a relationship between the uncritical Goldschmidt factor and the entropy change during the formation of perovskites from simple oxides.

II. LOW-TEMPERATURE SPECIFIC HEAT AND ENTROPY

1. Magnesium Titanates

$MgO{\cdot}TiO_2$. Shomate[5] measured the low-temperature specific heat of a $MgTiO_3$ sample containing 0.8% of $MgSiO_3$ in the temperature range 52.6–296.2 K. His values for the specific heat and the entropy at 298 K are 21.93 and 17.8 ± 0.1 cal $mole^{-1}$ K^{-1}, using the Debye and the Einstein function $D(365/T) + E(383/T) + 3E(711/T)$ for extrapolation to 0 K. An independent calculation using the same data[5] gave $S_{k,298} = 17.8230$ e.u. The value $S_{k,298} = 17.82 \pm 0.10$ e.u. (which is also adopted in Refs. 3 and 4) is therefore recommended. The enthalpy calculated from these results is $H_{298} - H_0 = 3239.2$ cal $mole^{-1}$, in good agreement with the tabulated value[3,4] 3240 cal $mole^{-1}$. The rounded-off value, with an uncertainty of ±20 cal $mole^{-1}$, is recommended. The standard specific heat of $MgTiO_3$ at 298 K is taken[3,4] to be 21.960 cal $mole^{-1}$: this value differs somewhat from that given by Shomate[5], but no explanation is given. Extrapolation of high-temperature enthalpy measurements[6] gives $C_{p,298} = 21.92$ cal $mole^{-1}K^{-1}$. The recommended value is $C_{p,298} = 21.96 \pm 0.03$ cal $mole^{-1}K^{-1}$.

$MgO{\cdot}2TiO_2$. The low-temperature specific heat of $MgTi_2O_5$ (99.5% purity) was measured by Todd[7] in the temperature range 52.5–296.4 K. Extrapolation to 0 K was carried out with the Debye and Einstein functions $D(264/T) + 4E(420/T) + 3E(906/T)$. The standard entropy of $MgTi_2O_5$ was rounded off to $S_{k,298} = 30.4 \pm 0.2$ e.u., although direct calculation gives 30.41 e.u. An independent calculation from the same results[7] gave $S_{k,298} = 30.415$ e.u. Ref. 4 gives the value 30.42 e.u., which agrees even better with the independent calculation. The JANAF tables[3] give a tentative value of $S_{k,298} = 32.41 \pm 1.5$ e.u. by allowing for the cation disorder at 0 K and for congruent melting of the compound $MgTi_2O_5$.

The correction for non-zero entropy at 0 K requires a detailed consideration of the crystal structure of $MgTi_2O_5$ and of the disposition of the cations in the polyhedra. Magnesium dititanate is stable with respect to $MgTiO_3$ and TiO_2 only at high temperatures, decomposing into geikielite and rutile at low temperatures. This effect arises from the possibility of disorder in the positions of the Mg^{2+} and Ti^{4+} ions in the crystallographically non-equivalent sites of $MgTi_2O_5$. If we assume that all the Mg^{2+} and Ti^{4+} ions are randomly located we must add $\Delta S = 3R \ln 2 = 3.79$ e.u. to $S = 30.41$ e.u. This gives us the best entropy value $S_{k,298} = 34.2$ e.u., which we shall use in the following calculations as well as the JANAF value[3]. If we assume that all the Mg^{2+} ions and one-half the Ti^{4+} ions are randomly positioned we obtain $S_{k,298} = 30.4 + 2.75 = 33.15$ e.u. X-Ray diffraction analysis of $MgTi_2O_5$ quenched from 1500°C indicates a distribution corresponding to the formula $(Mg_{0.684}Ti_{0.316})_{4C}{\cdot}(Mg_{0.316}{\cdot}Ti_{1.684})_{8t}O_5$, i.e. a disorder factor $x = 0.316$ ($x = 0$ for the normal cation distribution, $x = 2/3$ for a fully disordered distribution, and $x = 1$ for an inverted cation distribution).

Todd[7] obtained $C_{p,298} = 35.15$ cal $mole^{-1}$ K^{-1} for the standard specific heat of $MgTi_2O_5$. This value is adopted in Ref. 4: it is consistent with high-temperature enthalpy measurements[8] but it differs from the JANAF value[3] of 35.10. We recommend the value $C_{p,298} = 35.15 \pm 0.05$ cal $mole^{-1}$ K^{-1}.

Todd did not calculate the enthalpy of magnesium dititanate. A calculation from his results gives $H_{298} - H_0 = 5361$ cal $mole^{-1}$. The values 5363 and 5428 cal $mole^{-1}$ are given in Ref. 3 and 4 respectively: the latter value is inconsistent with the independent calculation of the entropy. We recommend the value $H_{298} - H_0 = 5360 \pm 40$ cal $mole^{-1}$.

$2Mg{\cdot}TiO_2$. The low-temperature specific heat of Mg_2TiO_4 ([MgTi]MgO_4 spinel, of 99.5% purity) was measured by Todd[7] in the temperature range 52.38–296.5 K. The results were extrapolated to 0 K by using the Debye and Einstein functions $D(305/T) + 3E(447/T) + 3E(823/T)$. He obtained a standard entropy of $S_{k,298} = 24.76 \pm 0.15$ e.u., which is exactly confirmed by an independent calculation using his results. Ref. 4 gives $S_{k,298} = 26.13$ e.u., and Ref. 3 gives 27.51 ± 1.5 e.u. The difference arises from different estimates of the configurational entropy due to disorder. Magnesium orthotitanate is an inverted spinel, with the magnesium ions in tetrahedral (A) and in octahedral (B) positions. The cation distribution can be expressed as Mg[MgTi]O_4, where the square bracket denotes the ions octahedrally surrounded by oxygen ions. Therefore the entropy obtained from specific heat data must be corrected by adding the ordering entropy of the cations in B positions ($2R \ln 2 = 2.75$ e.u.), which gives $S_{k,298} = 27.51$ e.u. This is the value which we recommend. We note that an intermediate value is quoted in Ref. 4, with an ordering correction of $R \ln 2 = 1.38$ e.u.

The standard specific heat quoted by Todd is $C_{p,k,298} = 30.76$ cal $mole^{-1}$ K^{-1}, with a probable error of ±0.02 cal $mole^{-1}$ K^{-1}. This value is consistent with high-temperature measurements of enthalpy[8], and differs only slightly from the value (30.75) adopted in Ref. 4.

The enthalpy of the orthotitanate was not computed by Todd. A calculation based on his results gives $H_{298} - H_0 = 4502$ cal $mole^{-1}$, which is identical to the value quoted i Refs. 3 and 4. We recommend the rounded-off value $H_{298} - H_0 = 4500 \pm 30$ cal $mole^{-1}$.

2. Calcium Titanates

$CaO{\cdot}TiO_2$. The low-temperature specific heat of $CaTiO_3$ (purity better than 99%) was measured by Shomate[5] in the range 52.5–296.3 K. Extrapolation to 0 K was made by using the sum $D(256/T) + 2E(375/T) + 2E(768/T)$. Shomate calculated $S_{k,298} = 22.38$ e.u. for the standard entropy of $CaTiO_3$, in very good agreement with an independent calculation based on his results and also with the JANAF value[4]. We recommend this value, with an uncertainty of ±0.10 e.u.

The standard specific heat of $CaTiO_3$ at 298 K was found[5] to be 23.34 cal $mole^{-1}$ K^{-1}. The same value is quoted in Refs. 4 and 9. Extrapolation from high-temperature measurements of enthalpy[6] gives 23.35 cal $mole^{-1}K^{-1}$. We recommend the value $C_p = 23.34 \pm 0.05$ cal $mole^{-1}K^{-1}$, the rather wide uncertainty reflecting the absence of corrections for impurities in the sample[5].

Shomate did not calculate the standard enthalpy of $CaTiO_3$. A calculation based on his results gives $H_{298} - H_0 = 3800.7$ cal $mole^{-1}$. We recommend the rounded-off value 3800 ± 20 cal $mole^{-1}$.

$3CaO{\cdot}2TiO_2$. The low-temperature specific heat of $Ca_3Ti_2O_7$ was measured by King[10] in the range 52.6 to 296.9 K. Chemical analysis of his sample gave 48.61% TiO_2 (theoretical value 48.71%). Extrapolation to 0 K was by the sum of functions $D(158/T) + 5E(333/T) + 5E(652/T) + E(781/T)$. The standard entropy recommended by King is $S_{k,298} = 56.1 \pm 0.4$ e.u., with which we concur. This value coincides, after rounding off, with the value (56.057 e.u.) obtained by an independent calculation from the same results[10]. It is also adopted in Ref. 4.

King's measurements[10] give $C_{p,298} = 57.20$ cal $mole^{-1}K^{-1}$ for the standard specific heat of $Ca_3Ti_2O_7$, with an uncertainty of ±0.05 cal $mole^{-1}$ K^{-1}. The enthalpy of the compound was not calculated by King, and is not given in Ref. 4. A calculation based on King's results gives $H_{298} - H_0 = 9418.6$ cal mole^{-1}. We recommend the rounded-off value $H_{298} - H_0 = 9420 \pm 70$ cal mole^{-1}.

3. Strontium Titanates

$SrO \cdot TiO_2$. $SrTiO_3$ undergoes four clearly defined low-temperature phase transformations of the second kind: at 0.06, 35, 65, and 107 K.

1) The transition from the high-temperature cubic structure to a tetragonal structure in the temperature range 100–110 K has been noted in more than 50 investigations.

The first report of this transition was made in 1956 by Gränicher[11], who noted anisotropy of the dielectric constant below 100 K, and subsequently by Müller[12], who observed tetragonal domains in $SrTiO_3$ crystals doped with Fe^{3+} by ESR measurements below 100 K. According to the ESR results[12-21] the low-temperature phase is tetragonal, with a c/a ratio of 1.0003 at 77 K. After a number of unsuccessful attempts[13,20,25] this structural change was demonstrated directly by X-ray diffraction[22-24]. However it was pointed out[26] that neither the axial ratio nor its temperature dependence[23] agrees with the ESR results. It was shown that the main contribution to the change in the pseudo-cubic structure with $c/a = 1.00008$ is a rotation of neighbouring oxygen octahedra around the original cubic axis[23]. The angle of rotation φ is treated as an ordering parameter for this phase transformation of the second kind. This conclusion was confirmed by neutron diffraction work[26-31]. The cubic structure of the $SrTiO_3$ perovskite is assigned O_h symmetry, and the low-temperature tetragonal structure D_{4h} symmetry[20,32,33]. The phase transformation is accompanied by marked changes in elastic constants[34-53], Rayleigh[38] and Raman spectra[32,33,54-59], double refraction[22,24], and by a decrease in the amplitude of the ^{87}Sr[60] NMR spectrum, increased thermal diffusivity and thermal conductivity[61], and a slight broadening of the ESR spectra of crystals containing magnetic impurities[12,13,15-21]. The high-temperature $SrTiO_3$ cubic structure is shown to be imperfect by the anisotropy of its electrical properties[11,62-66] and of the thermal stress[67,68]. The transition temperature varies with sample purity, pressure, and degree of reduction[46,47,69].

The mechanism of the transformation is discussed in almost all the above-mentioned papers. The most detailed analysis is given by Reshchikova[70], who assigns this $O_h \rightleftharpoons D_{4h}$ phase transition (accompanied by a fourfold increase in volume of the unit cell) to the displacement type of transition, arising from the presence of soft modes of lattice vibration in the cubic phase with a non-zero wave vector, which become "frozen" during the phase transition. Another group of papers deals with the mechanism of the transformation and with the structure of the equilibrium phases without attempting to specify the exact temperature of the transition[71-84]. Some workers failed to observe any anomalies in the electrical[85,86] and optical properties[87] in the transition region. Luthi and Moran[47] have discussed the reasons for this discrepancy.

The specific heat of $SrTiO_3$ has been measured directly in the transition region[61,66,69,88]. Garnier[69] found that the transition region extends over 2 K, and that T_{tr} is lowered by almost 1 K if the sample is annealed. The transition is also more gradual with an annealed sample. These effects are ascribed to a 0.05% decrease in the concentration of oxygen. Subsequently Salamon and Garnier[61] observed a change in specific heat at 110 K on a sample supplied by Sakudo and Unoki[65], and they also noted a 2% change in thermal diffusivity and a 1% change in thermal conductivity at the same temperature.

In most of these papers the anomalous changes in property are presented graphically, and the T_{tr} values are obtained by interpolation. Values indicated by the work of different authors range from 99.5 K[31] to 112 K.[34,35]. Averaging all the data on the temperature of this transformation gives 107.2 K. However we can identify a group of papers[17,26,30,47,48,61,67,69,88] in which special attention is paid to the precise measurements of T_{tr}, by a variety of methods. Averaging these results gives $T_{tr} = 106.9$ K. The difference between the two averages is less than the width of the transition region (2 K). Therefore we recommend the rounded-off value $T_{tr} = 107 \pm 3$ K. The quoted uncertainty encompasses most of the experimental data and corresponds to the scatter of results obtained with different samples.

2) The second low-temperature transition in $SrTiO_3$ is most clearly shown by measurements of the thermal hysteresis of $1/\epsilon$ (62 K[89], 65 K[65]), of double refraction (50 K[22], 60 K[24]), of X-ray diffraction (50 K[22], 55–65 K[23]), and of Raman (67 K[32]) and ESR spectra (65 K[21,90]). Below 65 K $SrTiO_3$ has a rhombic structure[23,32,65], of the D_{2h} type, with $a:b:c = 0.9998:1:1.0002$. Transition from the antiferromagnetic to the paramagnetic state has been demonstrated[91] experimentally: this could be due to conversion of the domain configuration in the sample from c-plate to a-plate[65].

By giving greater weight to the wider-ranging investigations[21,65,90] we select $T_{tr} = 65 \pm 5$ K as the recommended value. It should be noted that the existence of this transition is still controversial. It is not confirmed by spectroscopic measurements[33] or by studies of acoustic properties[49].

3) The Curie temperature has been obtained from measurements of the temperature dependence of dielectric constant[11,86,89,92-95], of neutron diffraction[96], of acoustic[34,45] and i.r. absorption[71], and of electrostriction[32,45,64,92-97]. The calculated values of T_C range from 28 K[96] to 50 K.[92] The transition has been observed experimentally only in three laboratories: Lytle[23] obtained $T_C = 35$ K from X-ray diffraction measurements, O'Shea and coworkers[32] observed a change in the Raman spectra at 34 K, and Sorge and Hegenbarth[98] obtained $T_C = 36$ K from measurements of elastic constants. From these results we recommend the value $T_C = 35 \pm 2$ K, in good agreement with the value (36.3 K) obtained by averaging all the above calculated and experimental results.

The only work which explicitly denies all phase transformations below 105 K is an acoustic investigation[49] at temperatures in the region 4–130 K. Bogdanov and coworkers[24] identified three temperature regions in which the double refraction of $SrTiO_3$ obeys different laws: 110–60, 60–20, and 20–4.2 K. The latter region has a maximum at 10 K, confirming a previous report[23]. We should stress that this observation has been repeated only once[22], again by measurements of X-ray diffraction and of double refraction. Hence the information on thermal characteristics in the region 4–20 K is insufficient for a recommended value to be selected. The limit of 20 K, which is only approximate, was taken from Ref. 24, where the parameter being measured was practically linear in the region 15–50 K. The results of Kirkpatrick and Müller[14] therefore would appear to confirm the existence of a phase transformation.

4) The superconductivity of $SrTiO_3$ was first observed by Schooley and coworkers[99]. In three monocrystalline samples, reduced in different ways, the temperature of the superconducting transition was found to be 0.1, 0.25, and 0.28 K. A subsequent series of investigations[100-104] established that superconductivity is present in $SrTiO_3$ samples doped with Nb as well as in reduced samples. The T_{tr} value depends on the concentration of charge carriers n_c in the region 8×10^{18}–5×10^{20} cm^{-3}. T_{tr} increases at first with n_c, reaching a maximum at intermediate values of n_c, and then decreases. The n_c values were measured by the Hall effect, and T_{tr} from the magnetic susceptibility and electrical resistivity of the samples. With reduced samples the T_{tr} maximum was found at 0.3 K, with Nb-doped samples at 0.4 K. The lowest value of T_{tr} was 0.06 K.[101] For many samples the width of the transition region was 0.1 K. The transition to the superconducting state has been observed also by measurements of low-temperature specific heat[105,106].

We choose as the recommended value of the transition temperature $T_{tr} = 0.06$ K, i.e. the value obtained[101] for a $SrTiO_3$ sample with the smallest deviation from stoichiometry, the smallest degree of reduction, and the lowest concentration of charge carriers ($n_c = 8 \times 10^{18}$ cm^{-3}). Allowing for the observed width of the transition region we estimate the uncertainty as ± 0.03 K. We note that the highest value ($T_{tr} = 0.3$ K) was obtained for $n_c = 7 \times 10^{19}$ cm^{-3}.

Todd and Lorenson[107] measured the low-temperature specific heat of $SrTiO_3$ over the widest temperature range (55–296 K). No anomalies could be detected in their plot of specific heat against temperature. Below 51 K the specific heat was determined by using the sum $D(182/T) + 2E(319/T) + 2E(776/T)$. For 298 K the authors obtained $C_p = 23.51$ cal mole K^{-1} and $S^0 = 26.0 \pm 0.2$ e.u. The C_p value coincides with the extrapolation from measurements of enthalpy at high temperature[108]. The good agreement with Refs. 107 and 108 is pointed out by Narayanan and Vedam[109], who obtained calculated values of C_V for the region 55–1800 K. Thus we can choose $C_{p,\,k,298} = 23.51 \pm 0.02$ cal mole^{-1} K^{-1} as the recommended value.

The specific heat has been measured in the region of the transition to the superconducting state[105,106,110] with $SrTiO_3$ samples containing different charge carrier concentrations. The temperature dependence of C_p obtained in this work over the narrow range 0.5–4.0 K, and also the value $\Delta S_{tr} = 0.12$ mJ mole^{-1} K^{-1},[105] are not suitable for calculating the entropy and enthalpy of stoichiometric $SrTiO_3$.

Many workers have found[50,61,66,68-70,88] that the change in specific heat in the region of the phase transition at 107 K is also negligibly small, amounting to 0.5–1.3% of the lattice contribution. These values are smaller than the error in the calculation of $H_{298} - H_0$ and S°_{298} introduced by the extrapolation to the low-temperature region.

From Todd and Lorenson's results[107] we calculate $H_{298} - H_0 = 4120$ cal mole^{-1} and $S_{298} = 25.98$ e.u. The latter value agrees well with that obtained by the authors[107]: the discrepancy is very small, and can be ascribed to differences in the computational methods. Hence we can adopt $S_{298} = 26.0 \pm 0.2$ e.u. as the recommended value. The quoted uncertainty undoubtedly allows for the entropies of the low-temperature phase transitions, which are accompanied by very small changes in C_p. To the same degree of confidence we can recommend the value $H_{298} - H_0 = 4120 \pm 40$ cal mole^{-1} for the enthalpy of $SrTiO_3$, which was not calculated by Todd and Lorenson[107].

$2SrO \cdot TiO_2$. The low-temperature specific heat of Sr_2TiO_4 was measured by Todd and Lorenson[111] in the temperature range 53.6–296.7 K on a sample of 99.5% purity. Extrapolation to 0 K was done by using the sum of functions $D(162/T) + 3E(280/T)$ and $3E(664/T)$. The standard entropy obtained[111] (38.01 e.u.) agrees exactly with an independent calculation based on their experimental results (38.013 e.u.). We choose $S_{k,298} = 38.0 \pm 0.3$ e.u. as the recommended value: the same value is tabulated in Ref. 4.

Todd and Lorenson's value[111] for the standard specific heat of Sr_2TiO_4 is $C_{p,298} = 34.34$ cal mole^{-1} K^{-1}, which agrees with the extrapolation from high-temperature measurements of enthalpy on the same sample[108], and is tabulated in Ref. 4. We adopt this as the recommended value, with an uncertainty of ±0.03 cal mole^{-1} K^{-1}.

The standard enthalpy of Sr_2TiO_4 has not been calculated before. Using the results of Ref. 111 we calculate $H_{298} - H_0 = 6060 \pm 60$ cal mole^{-1}, which we proposed as our recommended value.

4. Barium Titanates

$BaO \cdot TiO_2$. Barium titanate has five polymorphic modifications: trigonal $\xrightarrow{80°C}$ rhombic $\xrightarrow{5°C}$ tetragonal $\xrightarrow{120°C}$ cubic $\xrightarrow{1250°C}$ hexagonal, all three low-temperature modifications being pseudo-cubic because the differences in the positions of the ions are not large. We shall discuss these transitions individually.

1) The ferroelectric $BaTiO_3$ transition. Most of the work on the properties of $BaTiO_3$ has been done near 120°C (the temperature of the transition from the non-ferroelectric to the ferroelectric phase). The thermodynamic theory of this transition was developed by Ginzburg[112,113] and elaborated by other workers[114-116]. Ginzburg discusses two variants of the theory, corresponding to observed facts. According to the first variant the phase transition near 120°C should be treated as a transition of the second kind but approaching a transition of the first kind; according to the second variant it should be treated as a transition of the first kind but approaching the second kind. Some workers[114,117-127,278] have treated it as a transition of the first kind, others[108,112,115,116,128-136] as a transition of the second kind. In view of the strong discrepancies between the experimental results of different workers (for example, on the temperature dependence of the spontaneous polarisation, the constant in the Curie–Weiss law, the discontinuity in specific heat, the temperature of the transition, and its hysteresis), and in view of the strong dependence of the results on the method of preparation and on the purity of the samples, we can conclude that different types of transition were observed by different workers.

The method most commonly used to determine the transition temperature was dictated by the most outstanding feature of barium titanate: the temperature dependence of the dielectric constant, which was studied on ceramic[117-120,122,126,129,137-165] and on single-crystal samples[118,123,126,127,134,135,159-161,167-173] in different fields[138]. In parallel with this work, several authors carried out X-ray structural[124,130,142,146,152,164,166,167,174-183], crystallographic[118,142,166,184], thermochemical[108,122,123,128,133,144,148,151,153,154,185-187,279,280,281], differential thermal[121,125,175,186,188-190], and dilatometric studies[124,130,144,147,151,153,164,174,177], and measured the tangent of the loss angle[143,154,173], the spontaneous polarisability[126,167,191], the refractive index and the double refraction[118,167,169,176,179,182,192,193,283], the

ESR spectra[194], the acoustic properties[123,165,278], the ferromagnetic hysteresis[119,156], the thermal diffusivity[195], and the variation of the electric properties[114,136,166,170] and of the transition temperature[126,196,197] with pressure and with field, applied in different crystallographic directions.

Many of the reported values[133,138,140,141,148,155,177] of T_{tr} are clearly unacceptable and will not be considered further. This is specially true of values in the region of 80°C, which are reported as probably too low as a result of the presence of impurities in the samples. This transition appears to be particularly sensitive to heat treatment conditions[155] as well as to the purity of the sample, since some of the other transitions (e.g. in Ref. 148) agree well with data obtained elsewhere. The lowest values of T_{tr} are ascribed[144,175] to the impurity effect of the binders added to improve the sintering properties of the samples. One paper[149] stands alone in suggesting that the ferroelectric properties of barium titanate are due entirely to the presence of impurities: unlike every other sample previously examined in that laboratory[137,138,140,141], a sample of $BaTiO_3$ prepared from chemically pure compounds was found to have a dielectric permeability which was not only constant over a wide temperature range but also relatively small. Thus the pure sample of $BaTiO_3$ was a dielectric, but not a ferroelectric. We stress that this conclusion[149] has not been confirmed by the extensive subsequent work on a wide variety of sample types.

Hysteresis of the transition temperature has been observed repeatedly[117,119–121,124,125,142,151,153,154,169,176,177]: the hysteresis is more marked for the cubic than for the tetragonal modification[176]. The existence of a temperature region of coexistence of two phases, of width (10–11 K) depending on the thermal history of the sample[151,177], is well established, but Harwood[146] points out that this region extends over 1–2 K for monocrystalline samples and ~10 K for polycrystalline samples. Roi[117] observed an even wider transition region (104–128°C) for a ceramic sample. He suggests that a transition region of finite width should be present only in polycrystalline samples, in which the simultaneous transition in all the microcrystals of the ceramic is prevented by internal stresses. The widest reported transition region (110–135°C) was observed in a ceramic sample[153]. Meyerhofer[169] found hysteresis (4.3 K) in single-crystal $BaTiO_3$, and pointed out various possible types of transition kinetics as a function of the applied field. Cross[119] observed different transition temperatures in different parts of a polycrystalline sample.

The effect of impurities on the transition temperature has been shown by several workers[171,182,283], T_{tr} decreasing with increase in impurity concentration. Variations in T_{tr} have also been noted by other workers[126,128,144,151,155,281]. The dependence of T_{tr} on experimental conditions has been clearly demonstrated[144,146,151,154].

No regularity has been observed in the behaviour of the transition temperature on changing from ceramic to monocrystalline samples. For example, Shirane and Takeda[153] obtained T_{tr} = 127 and 115°C for a ceramic and a monocrystalline sample, whereas Samara[126] obtained 112.5°C for a ceramic sample and 118.0, 120.0, 111.0, and 122.5°C for a series of four monocrystalline samples.

Many workers[117,134,137,147,150,152,157,158,160–162,170,181,184,185,191,194,196,279,280,283] were not interested in locating the temperature of the transition, and did not quote its numerical value. In these cases we have made an estimate of the transition temperature by noting the extremum of the anomaly presented graphically by each author. The average of 98 reported values of T_{tr} and of our estimates, but rejecting some unacceptable values, is T_{tr} = 119.2 °C. By taking only the values obtained in special measurements of T_{tr},[108,114,118–130,135,136,138,139,142–146,151,153–156,159,163–169,171–176,178–180,182,183,186–193,195,197,198] and giving double statistical weight to the values obtained in investigations involving two or more methods[118,122,123,146,151,153,164,169], we obtain the average value T_{tr} = 119.6 °C. This is close to the transition temperature usually quoted by physicists (" in the neighbourhood of 120 °C").

Values of $T_{tr} \leqslant$ 115°C were probably obtained with relatively impure or imperfect samples, or may have been due to unsatisfactory measurement methods. We stress that higher values of T_{tr} correspond to smaller amounts of impurity. The mean of the values chosen by this criterion[108,114,118–130,135,136,138,139,142–146,153–155,159,163–169,171–174,178–180,182,183,187–190,192,193,195,197,198] is T_{tr} = 121.5°C. We take this as the recommended value for the transition temperature, with an uncertainty of ± 5 K which allows for the thermal hysteresis of the transition as well as the error in the measurements.

The heat of the ferroelectric transition has been obtained by direct calorimetric measurements[121–123,153,154,279], by DTA,[190] and from measurements of the temperature dependence of the thermal expansion coefficient in conjunction with the Clausius–Clapeyron equation[125–127,162,188,191]. The anomalous temperature dependence of the specific heat in the region of the transition has also been investigated[133,136,140,141,144,146,151,187,280], but these workers did not attempt to calculate ΔH_{tr} as they considered the method insufficiently accurate[151]. An estimate of ΔH_{tr} can nevertheless be made from the published graphs of C_p against temperature or from the maximum values of ΔC_p. The mean of 24 values obtained in this way is ΔH_{tr} = 53.5 cal mole^{-1}. By averaging only the direct thermochemical determinations of ΔH_{tr} [121–123,153,154,190,279] we obtain 48.1 cal mole^{-1}, and by averaging only the values obtained from the Clausius–Clapeyron equation we obtain 46.8 cal mole^{-1}. The last two values agree reasonably well. Estimates of ΔH_{tr} made from plots of C_p are very inaccurate (from 15 to 100 cal mole^{-1}) and should be rejected. We also reject the value given by Roberts[121] (ΔH_{tr} = 15 cal mole^{-1}) as the lower limit of the latent heat of the transformation, estimated from measurements of the temperature change which occurs when the transition is induced by applying an electric field under adiabatic conditions. Averaging the other 13 values gives ΔH_{tr} = 47.4 cal mole^{-1}. We choose as the recommended value ΔH_{tr} = 47.5 ± 3 cal mole^{-1}, where the quoted uncertainty describes the error in the calorimetric measurements. Using T_{tr} = 394.65 K we obtain ΔS_{tr} = 0.12 e.u. for the entropy of the transformation.

2) Low-temperature transitions of $BaTiO_3$. The temperatures of these transitions were determined by measurements of specific heat[107,122,123,153,154], by microscopic[166], X-ray diffraction[131,166,176,178,179,199–201], and dilatometric studies[135,153,177], and by measurements of dielectric constant[123,129,135–137,148,153,155,164,166,167,170,173,185,202–205], of piezoelectric[166], acoustic[148,159], optical[131,173,176,179,193,201,203,206,283], and magnetic properties[205,207], as well as by studies of NMR [194] and luminescence spectra[208]. Some workers[153,159,166,176,204,205] used monocrystalline samples. Some[203,208] examined only the low-temperature transition at −80°C, others[122,129,136,137,164,170,177,194] ignored it and studied the transition at a higher temperature in the region of 10°C. Much of the work is devoted to physical investigations, with the aim of explaining the anomalies in the physical properties. Little effort was devoted to determining exactly the temperature of the transition.

Many workers treat the transition as a phase transformation of the first kind[117] in spite of the λ-shaped plot of C_p against temperature. The lack of a definite latent heat compels us to treat the thermodynamic characteristics of these transitions as phase transformations of the second kind. A review[135] of the anomalous properties of $BaTiO_3$ identifies the low-temperature transition temperature with the Curie point.

By averaging all the data on the two transition temperatures we obtain $T_{tr} = -75.5$ and 4.58°C. Some of the values[153,154] were assigned a double statistical weight because they were obtained by several methods, and two values[107] ($T_{tr} = -71.55 \pm 0.2$ and 11.75 ± 0.2°C) were given triple weight because this was the only investigation aimed at absolute measurements of the specific heat of $BaTiO_3$. Our averaging did not include values which had not been directly quoted by the authors but estimated by us from published property-temperature plots[129,136,137,167,170,185,194,202,204,207,208]. We quote that the dilatometric measurements[177] failed to detect any anomaly between −10 and 20°C. Averaging the values obtained by calorimetric measurements[107,123,153,154] specially aimed at determining the transition temperature gives −72.75 and 11.43°C, whereas averaging all the other values gives −76.9 and 1.47°C. The discrepancy between the two sets of data is specially large for the transition at the higher temperature. Accepting only the calorimetric measurements, we recommend the values $T_{tr} = 11.4 \pm 5$°C = 284.55 ± 5 K and $T_{tr} = -73 \pm 5$°C = 200.15 ± 5 K. The quoted uncertainty allows for the thermal hysteresis of the transitions and for the scatter of the physical measurements.

The enthalpies of these transitions have been calculated[107,123,153,154] from the anomalies in the temperature dependence of the specific heat. The most careful calorimetric study of $BaTiO_3$, in the range from 53 to 103 K, was reported by Todd and Lorenson[107]. In the range 278–293 K they obtained $\Delta H_{tr} = 26$ cal mole^{-1}, and in the range 196–206 K $\Delta H_{tr} = 12$ cal mole^{-1}. An independent treatment of their results by the method described in Refs. 1 and 2 gives $\Delta H_{tr} = 22.635$ (278–293 K) and 13.03 cal mole^{-1} (180–210 K). The former value agrees well with Ref. 153, less well with Ref. 107, and badly with Refs. 123 and 144. Rejecting the latter two values and averaging the others we arrive at the recommended value $\Delta H_{tr} = 23.5 \pm 4$ cal mole^{-1} for the heat of the transition in the region of 278–293 K. The quoted uncertainty corresponds to the estimate made in Ref. 153. For the region 180–210 K we recommend $\Delta H_{tr} = 13 \pm 1$ cal mole^{-1} by averaging the values most consistent[107,154] with our calculation and rejecting an unacceptable value[153].

Low-temperature measurements[154] of C_p show considerable scatter and discontinuities, and they cannot easily be fitted to a "normal" curve. Results[282] for the range 2–37 K are presented only graphically. Hence we shall use only the data from Ref. 107 to calculate the enthalpy and entropy of $BaTiO_3$, together with the suggested[107] sum of functions $D(198/T) + 2E(351/T) + 2E(669/T)$ for extrapolating to the low-temperature region. Our calculation based on the data of Ref. 107 gives $S_{k,298} = 25.79$ e.u., and therefore we recommend the value $S_{k,298} = 25.8 \pm 0.2$ e.u. obtained in Ref. 107. The enthalpy of $BaTiO_3$ was not calculated[107]. From the published results[107] we calculate $H_{298} - H_0 = 4230$ cal mole^{-1}, and we recommend this value with error limits of ±40 cal mole^{-1}.

The standard specific heat at 298 K was found[107] to be 24.49 cal mole^{-1} K^{-1}. A different set of data[154] gives 24.31 cal mole^{-1} K^{-1} by interpolation. Extrapolation from high-temperature measurements of enthalpy[108] gives a value identical to that of Ref. 107. Hence we choose $C_{p,k,298} = 24.49 \pm 0.02$ cal mole^{-1} K^{-1} as the recommended value.

Blunt and Love[209] observed a dielectric loss peak at 70 K with a ceramic sample of $BaTiO_3$, but no anomaly in the dielectric constant. A large increase in coercive force at temperatures below 20 K was reported[210] for a multidomain sample. However a special investigation[203] failed to confirm these observations. Neither the dielectric constant nor the ferromagnetic hysteresis had any anomalies in the region from 4.2 to 180 K. Hence we are unable to recommend any values for transitions in this temperature range.

$2BaO \cdot TiO_2$. The low-temperature specific heat of Ba_2TiO_4 has been measured[111] in the temperature range 54–307 K with a sample of 99.2% purity. Extrapolation to 0 K was by the sum of functions $D(104/T) + 3E(207/T) + 2E(523/T) + E(858/T)$. The recommended[111] standard entropy $S_{k,298} = 47.0 \pm 0.5$ e.u. agrees very well with the value (46.92 e.u.) obtained by an independent recalculation.

Extrapolation of the high-temperature enthalpy measurements[108] on the same Ba_2TiO_4 sample gives a standard specific heat of $C_{p,k,298} = 35.647$ cal mole^{-1} K^{-1}. Unlike the corresponding results for $BaTiO_3$, $SrTiO_3$, and Sr_2TiO_4 this value differs significantly from the directly measured[111] value $C_{p,298} = 36.48$ cal mole^{-1} K^{-1}. We choose the latter as the recommended value, with an uncertainty of ±0.1 cal mole^{-1} K^{-1} to allow for this discrepancy and for the inadequate purity of the sample.

The standard enthalpy of Ba_2TiO_4 has not been calculated previously. We obtain $H_{298} - H_0 = 6842.8$ cal mole^{-1} by using the data of Ref. 111, and we propose the rounded-off value 6840 ± 60 cal mole^{-1} as the recommended value.

5. Mixed Barium and Strontium Titanates

$BaTiO_3 - SrTiO_3$. Todd and Lorenson[107] measured the specific heat of $Ba_{0.543}Sr_{0.457}TiO_3$ in the range 53–298 K. They obtained $C_{p,k,298} = 23.98$, which we accept as the recommended value with an uncertainty of ±0.02 cal mole^{-1} K^{-1}. The sum of functions $D(192/T) + 2E(399/T) + 2E(676/T)$ was used to extrapolate the results below 51 K. The entropy value obtained[107], $S_{k,298} = 27.4 \pm 0.2$ e.u., is recommended. This value includes an enthalpy of mixing of 1.37 e.u. An independent calculation based on the same data[107] gave good agreement when the C_p values at 45, 50, and 51 K were obtained by graphical interpolation, but not when they were computed using the functional sum. The authors[107] did not calculate the standard enthalpy. Our calculation, using their experimental data, gave $H_{298} - H_0 = 4210$ cal mole^{-1}: we recommend this value, with an uncertainty of ±40 cal mole^{-1}.

Calculation by a linear combination of the enthalpies of $BaTiO_3$ and $SrTiO_3$ gives $H_{298} - H_0 = 4180$ cal mole^{-1}, which agrees with the recommended value within the error limits. The temperature plot of the specific heat of $Ba_{0.543}Sr_{0.457}TiO_3$ does not show the two transition effects observed in $BaTiO_3$ in this temperature region. Measurements of dielectric constant[211] on various mixed titanates suggest the possibility of a transition at 248 K, the dielectric constant peak observed in $BaTiO_3$ at 393 K shifting gradually towards lower temperatures as the mole fraction of strontium titanate in solid solution increases. A special series of measurements[107] in the region 232–262 K failed to reveal any anomaly in C_p. The authors[107] point out that the temperature coefficient of the specific heat for the solid solution above 248 K is lower than expected, and this could be interpreted as anomalous behaviour. A very small anomaly was noted[279] in the plot of C_p against temperature for a sample of $Ba_{0.5}Sr_{0.5}TiO_3$ in the region 100–400 K. However no numerical values are quoted[279], and we are unable to make an estimate of the transition temperature.

$BaSrTiO_4$. The low-temperature specific heat of the $BaSrTiO_4$ solid solution was measured by Todd and Lorenson[111] in the range 53–296.5 K. The results were extrapolated to 0 K by using the sum $D(116/T) + 3E(239/T) + 3E(646/T)$. The calculated[111] value $S_{298} = 45.79$ e.u. coincides with our independent calculation based on the same data (45.795 e.u.). We therefore recommend the value $S_{k,298} = 45.8 \pm 0.4$ e.u., which includes the term $S_0 = 2.75$ e.u. calculated[111] on the assumption of a fully disordered distribution of Ba and Sr cations in the crystal lattice of the solid solution of their titanates.

For the standard specific heat we recommend the reported[111] value $C_{p,k,298} = 34.95$ with an uncertainty of ± 0.1 cal mole^{-1} K^{-1} (corresponding to the uncertainty previously suggested for Ba_2TiO_4).

From the published data[111] we calculate a standard enthalpy of 6477.9 cal mole^{-1}, and we recommend the rounded-off value $H_{298} - H_0 = 6480 \pm 60$ cal mole^{-1}. By assuming linearly additive enthalpies for these solid solutions we obtain $H_{298} - H_0 = 6450$ cal mole^{-1} for $BaSrTiO_4$, which agrees with the adopted value within the error limits.

6. Calcium, Strontium, and Barium Zirconates

$CaO \cdot ZrO_2$. King and Weller[212] measured the specific heat of $CaZrO_3$ in the range 52.81–296.10 K. The extrapolation to 0 K was done by using the sum of functions $D(233/T) + 2E(355/T) + 2E(722/T)$. The reported[212] value $C_{p,k,298} = 23.88$ is recommended, with an uncertainty of ± 0.02 cal mole^{-1}. The calculated[212] $S_{k,298}$ value was 23.92 e.u. (the value tabulated in Ref. 4). An independent calculation, using the same data[212], gave 23.915 e.u. The value recommended by the authors[212] is 23.9 ± 0.2 e.u. A calculation of the standard enthalpy of $CaZrO_3$ from King and Weller's results[212] gives 3991.5 cal mole^{-1}: we recommend the rounded-off value $H_{298} - H_0 = 3990 \pm 40$ cal mole^{-1}.

$SrO \cdot ZrO_2$. The same authors[212] measured the specific heat of $SrZrO_3$ in the range 53.4–295.8 K, extrapolating their results to 0 K by the sum of functions $D(177/T) + 2E(308/T) + 2E(678/T)$. We recommend their value[212] $C_{p,k,298} = 24.71$, with an uncertainty of ± 0.02 cal mole^{-1} K^{-1}. This value is adopted in Ref. 4. The reported[212] value of $S_{k,298}$ is 27.52 e.u.: our independent recalculation gives 27.533 e.u. The recommended value[212] is $S_{k,298} = 27.5 \pm 0.2$ e.u. (the value quoted in Ref. 4). The standard enthalpy calculated from the same results[212] is 4362.2 cal mole^{-1}: we recommend the rounded-off value $H_{298} - H_0 = 4360 \pm 40$ cal mole^{-1}.

$BaO \cdot ZrO_2$. King and Weller[212] also measured the specific heat of $BaZrO_3$ in the range 53.6–296.1 K, extrapolating their results to 0 K by using the sum of functions $D(144/T) + 2E(273/T) + 2E(692/T)$. They obtained[212] $C_{p,k,298} = 24.31$ cal mole^{-1} K^{-1}, which we recommend (with an uncertainty of ± 0.02). Their calculated value[212] of $S_{k,298}$ is 29.83 e.u., which agrees well with our independent recalculation (29.835 e.u.). We recommend the value $S_{k,298} = 29.8 \pm 0.2$ e.u. The same values of specific heat and entropy are adopted in Ref. 4. For the enthalpy of $BaZrO_3$ we recommend the value $H_{298} - H_0 = 4515 \pm 40$ cal mole^{-1}, calculated from King and Weller's results[212].

III. HIGH-TEMPERATURE SPECIFIC HEAT AND PHASE TRANSFORMATIONS

1. Magnesium Titanates

The high-temperature enthalpies of $MgTiO_3$ have been measured by drop calorimetry ("method of mixtures") in the range 298–1720 K,[6] those of $MgTi_2O_5$ and Mg_2TiO_4 in the range 298–1800 K.[8] The results are described by the equations

Compound	Equation (cal mole^{-1})	Precision
$MgTiO_3$	$H_T - H_{298} = 28.29\,T + 1.64 \cdot 10^{-3}T^2 + 6.530 \cdot 10^5/T - 10\,771$	0.4%
$MgTi_2O_5$	$H_T - H_{298} = 40.68\,T + 4.60 \cdot 10^{-3}T^2 + 7.35 \cdot 10^5/T - 15\,003$	0.3%
Mg_2TiO_4	$H_T - H_{298} = 35.96\,T + 4.27 \cdot 10^{-3}T^2 + 6.89 \cdot 10^5/T - 13\,412$	0.3%

No solid-state transformation have been detected in the magnesium titanates.

Table 1. Melting points of magnesium titanates.

$2MgO \cdot TiO_2$	$MgO \cdot TiO_2$	$MgO \cdot 2TiO_2$	Reference
1840	—	1680	250
—	—	1645	213
1732±10	1630±10	1652±10	214
1740±20*	1680±20*	1690±20	215–217
1756*	1630*	1662	218
1750±10*	1680±10*	1690±10	219, 220

*Incongruent melting.

Melting-point data for the magnesium titanates, obtained in studies of the $MgO-TiO_2$ phase diagram, are given in Table 1 in chronological order. The incongruent melting of $2MgO \cdot TiO_2$ and $MgO \cdot TiO_2$ was recognised in all the work after 1956.

For Mg_2TiO_4 we reject the result of Ref. 250, which is clearly too high, and that of Ref. 214, which assumes congruent melting: unsatisfactory methods were used in these investigations, especially in the MgO-rich region. In both cases the phase diagram was constructed from measurements with an optical pyrometer, relying on visual observation of melting. The difficulty of visually determining the melting point further complicated the problem (common to all these investigations) caused by the partial reduction of TiO_2 in spite of the presence of an oxidising atmosphere. The precision of these measurements depends on the viscosity of the melt (which is very high in the presence of an excess of MgO), on the composition of the melt, on the presence of a eutectic or a compound, and also on the skill of the experimenter. We note that the melting of $MgTiO_3$ was not even detected in Ref. 250. The mean of the other three values given in Table 1, obtained by a quenching method and with a hot-stage microscope, is $T_f = 1750$°C, which can be taken as the recommended value (with an uncertainty of ±15 K) for the incongruent melting point of Mg_2TiO_4 (equilibrium solid phase MgO). We note that Circular 500,[9] quoting Ref. 250, gives 1835°C as the recommended value.

For $MgTiO_3$ we can average all the data in Table 1 (rejecting Ref. 214) and we obtain $T_f = 1660$°C, which we propose as the recommended value of the incongruent melting point with error limits of ±20 K. Simple averaging is used because there is no reason to assign greater statistical weight to any of the results. The composition of the liquid phase is not specified—the equilibrium solid phase is $2MgO{\cdot}TiO_2$. The JANAF tables[3] give $T_f = 1953 \pm 20$ K, but the value obtained in Ref. 214 is also mentioned. Because of the subsequent, careful work by the quenching method we cannot agree with the JANAF recommendation[3].

By averaging all the values in Table 1 for $MgO{\cdot}TiO_2$ we obtain $T_f = 1670$°C which we propose as the recommended value, with an uncertainty of ±20 K, which includes almost all the experimental values. Circular 500,[9] quoting Ref. 250, gives $T_f = 1680$°C, and the JANAF tables[3], quoting Refs. 215–217, give $T_f = 1690 \pm 20$°C. We prefer to average all the experimental results, for the reasons given above under $MgTiO_3$.

The enthalpies of melting of $MgTiO_3$ and $MgTi_2O_5$ are given[3] as 21.6 and 35 kcal mole^{-1} by analogy with data on sodium titanates and calcium titanate silicates. In the absence of direct experimental determinations we cannot accept these as recommended values. We note that premelting effects, arising from disordering of the solid phase at temperatures below the melting point, could have a significant influence on the true enthalpy of melting.

2. Calcium Titanates

Naylor and Cook[6] measured the high-temperature enthalpy of $CaTiO_3$ in a drop calorimeter for the temperature range 298–1794 K. A phase transformation, with a heat of 550 cal mole^{-1}, was detected at 1530 K. The following enthalpy values were obtained for α- and β-$CaTiO_3$ respectively: $H_T - H_{298} = 30.47T + 0.68 \times 10^{-3}T^2 + 6.690 \times 10^5/T - 11\,389$ cal mole^{-1} (298–1530 K, 0.6%) and $H_T - H_{298} = 32.03T - 11\,197$ cal mole^{-1} (1530 to 1800 K, 0.2%). We can accept the quoted[6] values $T_{tr} = 1530$ K and $\Delta H_{tr} = 0.550$ kcal mole^{-1} as recommended values, with error limits of ±5 K and ±0.010 kcal respectively. The entropy of the transformations, according to these data, is 0.36 e.u. These characteristics of the $CaTiO_3$ transition are quoted in Ref. 9, whereas Ref. 3 does not list any phase transformation in calcium titanates.

The results of the most important thermal investigations of the CaO–TiO_2 system are compared in Table 2; the dashes denote absence of data from certain laboratories on certain compositions. Explicit statements concerning the presence or absence of a particular compound are also listed in Table 2.

Work prior to 1954 was largely fragmentary, and aimed mainly at establishing the presence of various compounds and their formation during heat treatment[222–223,225–228], or at estimating the melting points of various titanates[221,224,225] by visual observations of drop formation during melting. Work reported since 1954 is more complex, including critical analyses of previously published data and attempts to explain or eliminate inconsistencies.

The first X-ray structural study of the whole of the $CaO{\cdot}TiO_2$ system[229] was reported in 1954. Other measurement techniques used in that work included the quenching method, visual observation of the melting of specially prepared pellets in an oxy-hydrogen flame, and differential thermal analysis (up to 1720°C) coupled with microstructural analysis of the samples. Only two compounds were identified: their melting points are given in Table 2. Similar results were obtained[230] by the cone softening method, the compositions being identified by X-ray diffraction. It was noted that the compound $3CaO{\cdot}2TiO_2$ does not readily form below 1500°C, which explains the failure to detect this compound in some investigations (e.g. Ref. 225). Some workers[229] interpreted the diffraction patterns of intermediate compositions by assuming dissolution of CaO in the solid titanates. Others[230] deny this hypothesis, and assign more complex diffraction patterns to the stoichiometric titanate.

Table 2. Reported compound formation and thermal data for the CaO–TiO_2 system (m.p., °C).

Eutectic with TiO_2	$Ca_2Ti_3O_8$	$CaTiO_3$	$Ca_4Ti_3O_{10}$	$Ca_3Ti_2O_7$	Ca_2TiO_4	Ca_3TiO_5	Ca_4TiO_6	Eutectic with CaO	Method**	Reference
1400	no	1740	—	—	—	—	—	1620	1	221
—	yes	yes	—	yes	no	no	no	—	2	222
1437	no	yes	—	—	—	—	—	—	3	223
1410	no	1970	—	—	1800	1870	no	—	4	224
—	no	1725	—	yes	no	—	no	—	2,5	225
—	no	yes	—	no	no	no	no	—	2	226
—	—	yes	—	yes	no	no	—	—	2	227
—	—	—	—	yes	—	—	—	—	6,7	228
1460	no	1954	—	1750	no	no	no	—	1, 3, 6	229
1475	no	1915	—	1750*	no	no	no	1725	1,6	230
—		—	1755	1740*	—	—	—	—	1,6	231
—	—	yes	no	yes	—	—	—	—	6	232
1460	no	1989	1870	—	no	no	no	1740	8	233, 234

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*Incongruent melting, equilibrium solid phase $CaTiO_3$.
**The numbers denote: 1) visual observation, 2) heat treatment, 3) quenching method, 4) visual observation of drop formation, 5) observation of drop formation in a H_2–O_2 flame, 6) X-ray diffraction analysis, 7) petrological study, 8) hot stage microscopy.

More recently Roth[231] extended previous work[230] by analysing the diffraction patterns of mixtures[229] in this system and comparing them with data for the SrO–TiO_2 system. He concluded that an additional compound is formed, of composition $4CaO{\cdot}3TiO_2$, rather than solid solutions. Roth demonstrated the thermodynamic stability of this compound by special X-ray studies of samples annealed at, or quenched from, 1550–1745°C. Relative measurements of the melting points of $3CaO{\cdot}2TiO_2$ and $4CaO{\cdot}3TiO_2$ gave incongruent melting points of 1740 and 1755°C respectively. These results were confirmed by visual observations of melting in different atmospheres and by the quenching method. Roth used these results to correct previously published phase diagrams[229,230].

Imlach and Glasser[232], in their study of the CaO–TiO_2–Al_2O_3 phase diagram, re-checked the work of Roth[231] and concluded that the compound $4CaO{\cdot}3TiO_2$ does not exist. Their X-ray work showed that slightly different diffraction patterns are obtained by varying the heat treatment procedure, suggesting a definite homogeneity region for the compound $3CaO{\cdot}2TiO_2$. Their ternary phase diagram[232] uses values identical to those of Ref. 229 for the binary CaO–TiO_2 system.

Jongejan and Wilkins[233] published a critical analysis of the phase diagrams and the experimental methods previously reported[229-232], and they pointed out that liquidus temperatures cannot be accurately determined by the visual method because of the difficulty of discerning the disappearance of the last crystals, particularly since the dendritic CaO crystals tend to float in the melt. They constructed a phase diagram[233] from observations in a hot-stage microscope. In addition to the congruently melting $CaTiO_3$ they detected $4CaO\cdot3TiO_2$, which melts incongruently at 1870°C (equilibrium solid phase $CaTiO_3$). The possibility that this temperature could apply merely to a solid-state transformation of $CaTiO_3$ is admitted[233], but a specially detailed study of the liquidus line in the TiO_2-rich region confirmed the existence of the compound $4CaO\cdot3TiO_2$. The incongruently melting compound $3CaO\cdot2TiO_2$ was also assumed to be present, but the solidus line was not accurately studied in this region and a break in the liquidus line was not detected. The composition ordinate for this compound and the liquidus line in the same region are shown as broken lines in the phase diagram. These results[233] were confirmed in a later paper[234].

The existence of the compound $CaO\cdot TiO_2$ is indicated by all the data on the $CaO-TiO_2$ system listed in Table 2. Among the melting-point data for this compound those from Refs. 221 and 225 are clearly unacceptable; this is not surprising in view of the inaccurate methods used. By averaging the remaining values we obtain $T_f = 1957$°C. Our recommended value is rounded off to $T_f = 1960 \pm 30$°C, the suggested uncertainty including most of the experimental data and reflecting the low precision of work at these very high temperatures.

The reported[222] existence of the compound $2CaO\cdot3TiO_2$ should be treated as unconfirmed.

Information on the CaO-rich part of the $CaO-TiO_2$ phase diagram is even more complex and contradictory.

The compound $4CaO\cdot TiO_2$ was not detected in any of the investigations which included this composition. The titanates $2CaO\cdot TiO_2$ and $3CaO\cdot TiO_2$ are indicated in one phase diagram[224], but melting points are not quoted, and the values in Table 2 were simply read off the diagram. All the other workers (see Table 2) deny the existence of these titanates. We must conclude that it would be premature to attempt a recommendation on their melting points.

Most of the structural studies which have been reported point to the existence of the compound $3CaO\cdot2TiO_2$, melting incongruently at a well defined temperature[229-231]. The temperature reported[233] as the melting point of the eutectic with CaO (1740°C) may have been a misinterpretation of the incongruent melting of $3CaO\cdot2TiO_2$. Basing our choice on the work of Roth[231], who made a special comparative study of the melting points of the neighbouring compositions $4CaO\cdot3TiO_2$ and $3CaO\cdot2TiO_2$ by several methods, we propose $T_f = 1740 \pm 15$°C as the recommended value for the incongruent melting point of $3CaO\cdot2TiO_2$. The suggested error limits include the other reported values[229,230]. The equilibrium solid phase is taken to be $CaTiO_3$, as shown by the following arguments.

The existence of the compound $4CaO\cdot3TiO_2$, discussed in three publications, is more controversial. Some deny it[232] on the basis of a special X-ray study and of the results[229] of De Vries and coworkers. On the other hand Roth[231] convincingly proves its existence by combining the same results[229] with those of his own investigations. However the break in the liquidus line[233] cannot be ascribed unequivocally to incongruent melting of a compound of the same composition. Furthermore the incongruent melting point of $4CaO\cdot3TiO_2$ quoted in Ref. 233 differs by more than 100 K from that quoted in Ref. 231, even though the latter phase diagram[231] agrees in other respects with those of other workers. We should add that the liquidus line of Ref. 233 does not show a break for the compound $3CaO\cdot2TiO_2$, in direct contradiction to other reports[229-232]. The authors[233] also cannot explain the serious discrepancy in their melting point for the eutectic composition rich in CaO. Because of all these inconsistencies we must conclude that the proof[233] of the existence of the compound $4CaO\cdot3TiO_2$ is not entirely convincing. Equally, there are no grounds for accepting the results of Ref. 231 in preference to the more recent results of Ref. 232. We must therefore await more definite confirmation of the existence of the compound $4CaO\cdot3TiO_2$, and more precise measurements of its phase characteristics.

Borisenko and Shirokova[235] observed a polymorphic transition at 765°C in their study of the compound $3CaO\cdot2TiO_2$ by a complex thermal analysis method. The thermal effect was small, and no volume change was detected. A structural study by X-ray ionisation analysis at 700 and 800°C revealed only a small change in the degree of tetragonal distortion of the lattice in this temperature range. An alternative explanation of the reported effect is possible, based on kinetic arguments. For example, a slight dependence of crystal structure on heat treatment conditions has been noted[232]. This transition is not confirmed by any of the other investigations by X-ray diffraction or thermal anslysis, and therefore we cannot include the transition temperature quoted in Ref. 235 in our list of recommended values.

3. Strontium Titanates

$SrO\cdot TiO_2$. No solid-state transformations have been observed in the measurement[108] of the enthalpy change $H_T - H_{298}$ for $SrTiO_3$. In the region 298–1800 K the results are described by the expression[108] $H_T - H_{298} = 28.23T + 0.88 \times 10^{-3}T^2 + 4.66 \times 10^5/T - 10\,058$ (cal mole^{-1}). The melting point of $SrTiO_3$ has been measured only in one laboratory[236,237], using a combination of thermal, X-ray diffraction, and microscopic methods[237], and found to be $T_f = 2040 \pm 20$°C. This must be taken as the recommended value in preference to the estimated values 2100°C [109] and 1910°C.[238]

Sr_2TiO_4. The high-temperature specific heat of Sr_2TiO_4 also was measured[108] in the range 384–1831 K. Between 298 and 1800 K the experimental results are described with 0.4% precision by the expression $H_T - H_{298} = 38.45T + 1.92 \times 10^{-3}T^2 + 4.67 \times 10^5/T - 13\,201$ (cal mole^{-1}).

An earlier[236] phase diagram for the $SrO-TiO_2$ system shows a maximum in the liquidus curve corresponding to the composition Sr_2TiO_4 ($T_f = 1800 \pm 20$°C). A more detailed investigation by the same authors[237] produced a revised phase diagram for the $SrO-TiO_2$ system in the composition range 33–100 mole % TiO_2. The left-hand boundary of this diagram corresponds to Sr_2TiO_4, with $T_f = 1860 \pm 20$°C, but the authors[237] do not discuss the type of melting or the discrepancy with their previous result. A polymorphic $\alpha-\beta$ transformation with $T_{tr} = 1600 \pm 10$°C is also reported[237] for Sr_2TiO_4.

A microstructural study[238] of the $SrO-TiO_2$ system has confirmed the stability of Sr_2TiO_4 up to T_f. A sample quenched from 1860°C showed signs of melting and traces of SrO. A polymorphic transformation was observed between 1500 and 1550°C. The structure of the samples was studied after a first anneal at 1600°C and a second anneal at 1500°C for 75 h or at 1550°C for 10 h. The first sample had the low-temperature structure, the second had the high-temperature structure. This work achieved a closer approach to equilibrium than that of Ref. 237, in spite of the large temperature step. Hence we take $T_{tr} = 1525 \pm 20°C$ as the recommended value. We note a slight discrepancy with the high-temperature enthalpy measurements of Coughlin and Orr[108], who did not attempt to detect polymorphic transformations. Since our adopted T_{tr} value lies at the boundary of the temperature range covered in Ref. 108 it is not surprising that equilibrium was not achieved in that work. Alternatively, the transition could have been masked by the interpolation procedure used in the drop calorimeter technique.

The results of Refs. 237 and 238 for the melting point of Sr_2TiO_4 are satisfactorily consistent, but those of Ref. 236 are unconfirmed. Therefore we take $T_f = 1860 \pm 20°C$ as the recommended value.

$Sr_3Ti_2O_7$. Drys and Trzebiatowski[237] detected, in addition to strontium meta- and orthotitanate, the compound $Sr_3Ti_2O_7$, which decomposes into solid strontium meta- and orthotitanate at 1640 ± 10°C. The decomposition temperature was determined by X-ray diffraction analysis of samples annealed at 1630, 1640, 1650, and 1660°C. The first two samples consisted of $Sr_3Ti_2O_7$, the last two of a two-phase mixture of $SrTiO_3 + Sr_2TiO_4$. The existence of $Sr_3Ti_2O_7$ was confirmed by microstructural studies[238], but the decomposition temperature was found in the range 1550–1600°C. A sample heat treated at 1600°C and again annealed for 10 h at 1550°C contained only $Sr_3Ti_2O_7$, whereas a sample annealed at 1600°C showed the presence of metatitanate and of the high-temperature form of Sr_2TiO_4. The work of Ref. 238 was done under conditions more closely approaching equilibrium. We therefore accept these results, and we give $T_{tr} = 1580 \pm 20°C$ as the recommended value for the decomposition temperature of $Sr_3Ti_2O_7$ into $SrTiO_3$ and β-Sr_2TiO_4.

Sr_3TiO_5. Cocco and Massazza[238] found yet another compound in this system: $3SrO{\cdot}TiO_2$, stable in the region of 1560–1760°C. Thus, a sample annealed at 1550°C contained Sr_2TiO_4 and SrO, a sample annealed at 1600 or 1750°C contained only the phase Sr_3TiO_5, and a sample annealed at 1770°C again consisted of SrO and Sr_2TiO_4. The transformation temperatures quoted by the authors[238], T_{tr} = 1560 and 1760°C, are recommended with an uncertainty of ±20 K. We note that this region of compositions was not examined in Ref. 237.

4. Barium Titanates

$BaTiO_3$. The high-temperature enthalpy of $BaTiO_3$ was measured[108] in the range 400–1800 K: $H_T - H_{298} = 29.03T + 1.02 \times 10^{-3}T^2 + 4.58 \times 10^5/T - 10\,282$ cal mole^{-1} (0.3% precision).

The melting point of $BaTiO_3$ is generally agreed[180,183,239–243] to lie in the range 1610–1620°C. There is only one substantially different value: T_f = 1700°C, reported in Ref. 244 and quoted in Refs. 108 and 135. The shortcomings of the method[244] are discussed in Ref. 241. By averaging all the values except that of Ref. 244 we obtain the recommended value $T_f = 1616 \pm 5°C$.

The high-temperature transition of $BaTiO_3$ from the perovskite to the hexagonal structure has been studied by microscopic[180,183,239], thermal[180,183,239,240,243], X-ray diffraction[183,240,243], and kinetic methods[245]. The dependence of the transition temperature on impurity concentration and on heat-treatment atmosphere was investigated by Glaister and Kay[242]. With two exceptions[239,245], giving a transition temperature of 1450°C, all the other workers give T_{tr} = 1460°C. The discrepancy arises from the different temperature intervals chosen for the heat treatment experiments (50 K in Ref. 239). We recommend the value $T_{tr} = 1460 \pm 5°C$. It should be noted that a series of enthalpy measurements up to 1800 K [108] failed to reveal any thermal effect in the neighbourhood of T_{tr}.

$BaTi_2O_5$, $BaTi_3O_7$, $BaTi_4O_9$. The liquidus diagram of the $BaO–TiO_2$ system was first reported in 1951 by Statton[244], who used an optical pyrometer to study the melting of various compositions on a molybdenum strip in a vacuum. The diagram shows clear peaks for $BaTi_2O_5$ (1675°C), $BaTi_4O_9$ (1640°C), and also for $BaTiO_3$ and Ba_2TiO_4, but the graphical presentation is not accompanied by numerical tabulations. Corrections had to be applied for the interaction of BaO with Mo, which affected the results. All the compounds were identified by X-ray diffraction.

Trzebiatowski and coworkers[239] constructed the phase diagram of this system in the composition region 33 to 100 mole % TiO_2. They used visual and differential thermal analysis methods, combined with microscopic and X-ray studies of the quenched samples. They quote 1315 and 1465°C respectively for the congruent melting points of $BaTi_2O_5$ and $BaTi_4O_9$, but congruent melting is not clearly shown in their diagram. Furthermore the presence of the compound $BaTi_3O_7$ is suggested both by the liquidus curve in the region of ~75 mole % TiO_2 and by the diffraction pattern of this composition.

Rase and Roy[240] made a careful study of the phase composition of the $BaO–TiO_2$ system at high temperatures, and analysed the results of previous work in great detail. From their study of quenched samples, and their visual and thermographic observations of melting on a platinum strip, they obtained the phase diagram of the system and they established methods of preparing the compounds in polycrystalline or monocrystalline forms, as well as their stability conditions. The existence of $BaTi_2O_5$ and $BaTi_4O_9$ was confirmed, but these compounds were found to melt incongruently at 1322 and 1428°C respectively. The equilibrium solid phases are reported to be $BaTiO_3$ and TiO_2 respectively. The same workers[240] also convincingly identified the compound $BaTi_3O_7$, with T_f = 1357°C (equilibrium solid phase $BaTi_4O_9$). We take this as the recommended value, with error limits of ±10 K.

Shchepochkina[241] critically discussed the experimental shortcomings of Statton's work[244] and obtained more precise values of the phase transition temperatures in the $BaO–TiO_2$ system by a method relying on the softening of rod tips. For $BaTiO_3$ she obtained T_f = 1615°C, which is very close to our recommended value of 1616°C, and for the congruent melting of $BaTi_2O_5$ and $BaTi_4O_9$ she obtained 1385 and 1445°C respectively.

Judging by the general standard of the work, both in quality and in quantity, we accept the result of Rase and Roy[240], and we conclude that the melting of barium dititanate and tetratitanate is incongruent. Statton's results[244] are clearly inconsistent with later work, probably because of the serious compositional changes aggravated by the use of a vacuum and by the incongruent melting of the samples. Comparison of the T_f values for $BaTiO_3$, given as 1610°C in Ref. 239 and 1618°C in Ref. 240, with the recommended value of 1616°C suggest the possibility of a large systematic error in Ref. 239. We note that Statton obtained an unacceptable value (T_f = 1700°C) even for $BaTiO_3$. By averaging the results of Refs. 239, 241, and 240, but giving the latter a doubtful statistical weight, we arrive at the rounded-off temperatures 1340 ± 20 and 1440 ± 15°C for the incongruent melting of $BaTi_2O_5$ and $BaTi_4O_9$, which are recommended. The different uncertainty limits reflect the reproducibility of the two sets of results.

Ba_2TiO_4. The incongruent melting point of the orthotitanate in Statton's liquidus diagram[244] is 1692°C. T_f values of 1820, 1860, and 1880°C are obtained in Refs. 239, 240, and 241 respectively. The experimental details of the procedures used are discussed above. Rase and Roy[240] consider Ba_2TiO_4 to be too reactive towards platinum at its melting point for a reliable identification of the type of melting. The increase in the T_f value from Ref. 244 to Ref. 241 does not line up with the results of those same workers for $BaTiO_3$ and other titanates, and it is difficult to select any particular value as the preferred one, especially in view of the experimental difficulties and of the very high value of T_f. However Statton's value[244] is probably unacceptable. By averaging the other values, giving double weight to Rase and Roy's[240], we arrive at the recommended value T_f = 1855 ± 20°C.

The high-temperature enthalpy of Ba_2TiO_4 has been measured[108] in the range 398–1831 K by a drop calorimeter method. No solid-phase transitions were noted. The experimental results are described with a precision of 0.6% by the expression $H_T - H_{298} = 43.00T + 0.80 \times 10^{-3}T^2 + 6.96 \times 10^5/T - 15\,226$ (cal mole^{-1}).

5. Magnesium Zirconate

The existence of the compounds $MgO \cdot ZrO_2$ and $2MgO \cdot 3ZrO_2$ has been suggested by a structural study[263] of the $MgO-ZrO_2$ system. The liquidus line of the $MgO-ZrO_2$ system given in Ref. 254 on the basis of a visual thermal study differs from that of Ref. 263: the compound $2MgO \cdot 2ZrO_2$ is not found on the liquidus line, and the compound $MgZrO_3$ has a congruent melting point. The melting point is not quoted, but it can be estimated from the published diagram as T_f = 2130°C. Circular 500,[9] quoting Ref. 254, gives T_f = 2120°C. Von Wartenberg[250], referring to his previous work[254,264], gives T_f = 2150°C. We note that the melting of magnesium zirconate was not studied in Ref. 264.

All these values originate from the same laboratory. Our recommended value is obtained by averaging them: T_f = 2130 ± 20°C. The suggested uncertainty allows for the likely error in the various estimates.

6. Calcium Zirconates

$CaZrO_3$. The values reported by different authors for the congruent melting point of $CaZrO_3$ are in good agreement: 2350°C,[246,247] 2325°C,[248] and 2370°C.[249] We take their mean as the recommended value: T_f = 2350 ± 20°C.

The high-temperature enthalpy of $CaZrO_3$, measured[251] in a drop calorimeter, was found to be $H_T - H_{298} = 30.41T + 0.62 \times 10^{-3}T^2 - 3.46 \times 10^5/T - 10\,290$ cal mole^{-1} (0.8%) for the range 491–1066 K. No phase transformations were observed in this temperature region.

X-ray structural analysis[252] revealed two modifications of $CaZrO_3$: a low-temperature form, stable below 1200°C, and a high-temperature form, stable above 1250°C. The transition was found to be gradual[252], occurring in the range 1100–1250°C on heating and in the range 1100–900°C on cooling the sample. The authors conclude[252] from published data that the lattice parameter of this compound depends on the temperature at which the sample was synthesised. These results are semi-quantitative and cannot be used as a basis for a recommendation on this phase transformation.

$CaZr_4O_9$. Garvie[253] carried out an X-ray structural analysis of the $CaO-ZrO_2$ system along the 1305, 1400, 1500, 1600, 1700, and 1765°C isotherms in the region rich in CaO. The variation of lattice parameter with composition revealed a sharp boundary to the formation of cubic solid solutions of CaO in ZrO_2 at 20 mole % CaO, corresponding to the compound $CaZr_4O_9$. The change in lattice parameter of this composition at ~1650°C is interpreted by Garvie as a phase transition giving a different defect structure. The existence region of $CaZr_4O_9$ in the phase diagram lies above 1270°C: below this temperature the co-existing phases are ZrO_2 and $CaZrO_3$. The recommended temperatures for the equilibrium formation and for the phase transformation of $CaZr_4O_9$ are 1270 ± 30 and 1650 ± 30°C respectively.

7. Strontium Zirconates

$SrZrO_3$. The congruence of the melting of $SrZrO_3$ was shown in Ref. 254, but the authors found the melting point inaccessible and estimated it as above 2600°C.

Berezhnoi and Belik[255] quote T_f = 2750°C for $SrZrO_3$ without disclosing the method of measurement. The same value was obtained by Travers and Foex[249], who used a solar furnace to study the $SrO-ZrO_2$ phase diagram. Noguchi and coworkers[256] also used a solar furnace in their work on the liquidus curve of the $SrO-ZrO_2$ system, and obtained T_f = 2646 ± 20°C for $SrZrO_3$.

Both these phase diagrams[249,256] indicate congruent melting of the compound $SrZrO_3$. However the melting point given in Ref. 256 is inconsistent with those of Ref. 255 and with the independent measurements of Ref. 249, and therefore we take as our recommended value T_f = 2750 ± 20°C. We note that Carlsson's review[259] gives the melting point of $SrZrO_3$ as approximately 2800°C.

Berezhnoi and coworkers[260] calculated the enthalpy and entropy of melting of $SrZrO_3$ from the phase diagram of the $SrO-ZrO_2$ system: 16.7 kcal mole^{-1} and 5.5 e.u. We recommend their ΔH_f value with an uncertainty of ±2 kcal mole^{-1}. The corresponding value of the entropy of melting is ΔS_f = 5.52 e.u.

Carlsson[259] investigated the high-temperature solid-phase transitions of $SrZrO_3$. Differential thermal analysis at 550–950°C gave two endotherms corresponding to transitions at 730 and 860°C. These measurements are found to be poorly reproducible. The transition temperature is assumed to be the point at which the heating curve begins to deviate from its normal shape. The presence of different crystal structures at 600, 820, 1000, and 1200°C was confirmed by high-temperature X-ray diffraction. A rhombic modification was found to exist from room temperature up to 700°C, when it converts into a pseudo-tetragonal form with $c/a < 1$. Above 830°C another pseudo-tetragonal modification is formed, with $c/a < 1$, and at 1170°C the structure becomes cubic. Carlsson quotes the temperatures of the first two transitions, from DTA results, as 730 ± 25 and 860 ± 25°C, stressing the satisfactory agreement with the X-ray results. The temperature dependence of the lattice parameters was studied for the high-temperature transition with T_{tr} = 1170°C. The plot of dielectric constant against temperature has a peak at ~700 and 850°C. The transformation at 1170°C is thought to be either ferroelectric–paraelectric or antiferroelectric–paraelectric, the latter being the more likely. The temperature dependence of electrical resistance of $SrZrO_3$ has no anomaly at 1170°C, though the compound behaves as a semiconductor above 1000°C.

Peaks at 762, 846, and 1095°C have been reported[261] on the DTA curve of $SrZrO_3$ (the quoted temperatures corresponding to the peak maxima, unlike those of Carlsson[259]). The same reference shows breaks at 745, 1060 (very weak), and 1480°C in the temperature dependence of electrical resistance.

The T_{tr} value of the low-temperature transition[261] agrees well with Carlsson's value[259] in view of the different methods of identifying the transition point on the DTA curve. Therefore we choose T_{tr} = 730 ± 25°C as the recommended value. The two sets of data for the second transition are also in very good agreement: we choose T_{tr} = 860 ± 25°C. For the last transition we average the DTA value[261] and the value obtained[259] from the temperature dependence of the lattice parameters, and we obtain T_{tr} = 1135 ± 35°C as the recommended value.

Further confirmation is needed of the possible transition at 1480°C [261] suggested by the electrical resistance curve, because it occurs at the very limit of the temperature range of the experiment, and it has not so far been detected by any other method.

The high-temperature enthalpy of $SrZrO_3$ has been measured by drop calorimetry[284] at temperatures in the range 562–2318 K. The results are described with 0.3% precision by the expression $H_T - H_{298} = 147.072T - 2.077 \times 10^{-3}T^2 + 4.148 \times 10^6/T - 57\,277$ (J mole^{-1}). Other workers[285] used the same method in the range 298–1620 K and obtained the following expression (1% precision): $H_T - H_{298} = 29.79T + 0.70 \times 10^{-3}T^2 + 4.89 \times 10^5/T - 10\,584$ (cal mole^{-1}). Neither of these investigations detected the polymorphic transformations of $SrZrO_3$, obviously because of the rather large temperature step between the measurements (80–120°C). Furthermore the accuracy of these results is in doubt, the former[284] being higher than the latter[285] by 5.7–7.1% in the range 700–1600 K. We should also note that existing information on the polymorphic transformations of $SrZrO_3$ is completely ignored in both these publications[284,285].

Sr_2ZrO_4, $Sr_3Zr_2O_7$, $Sr_4Zr_3O_{10}$. Noguchi and coworkers[256] studied the liquidus diagram of the $SrO–ZrO_2$ system with a solar furnace. The phase composition of the samples was checked by chemical analysis and by X-ray diffraction after quenching. The evaporation rate of some of the samples was also measured. Three compounds were found in the system in addition to $SrZrO_3$: Sr_2ZrO_4, $Sr_3Zr_2O_7$, and $Sr_4Zr_3O_{10}$. The congruent melting points of Sr_2ZrO_4 and $Sr_4Zr_3O_{10}$ are given as 2325 and 2674°C respectively. We take the latter value as the recommended T_f for $Sr_4Zr_3O_{10}$, with an uncertainty of ±20 K.

Travers and Foex[249] also studied the $SrO-ZrO_2$ phase diagram by differential thermal analysis, using a solar furnace. Special attention was paid to the compound $SrZrO_3$. The compound $Sr_4Zr_3O_{10}$ is not shown on their phase diagram, and Sr_2ZrO_4 and $Sr_3Zr_2O_7$ are stated to melt incongruently. T_f = 2250°C is quoted for $Sr_3Zr_2O_7$, and the melting of Sr_2ZrO_4 is shown as a broken line on the diagram, from which we estimate T_f = 2220°C. It is stressed[249] that all the compounds were identified by X-ray diffraction.

Evidence on the type of melting of Sr_2ZrO_4 is contradictory[249,256], and therefore we cannot give a ruling on this problem. However the direct experimental determination[256] should be the more reliable. We therefore recommend, after rounding off, T_f = 2300 ± 30°C for the melting point of Sr_2ZrO_4.

The compound $Sr_3Zr_2O_7$ was first identified[262] after heating the corresponding mixture at 1700°C. Noguchi and coworkers[256] obtained the same diffraction pattern after a similar preparation. However a 2 hour anneal at 1800 and 1900°C followed by air quenching gave only the diffraction lines of $Sr_4Zr_3O_{10}$, with small amounts of $SrZrO_3$ and SrO. The stability region of $Sr_3Zr_2O_7$ therefore appears to extend only up to 1700°C.[256] This region is shown as a broken line in the phase diagram[256], $Sr_3Zr_2O_7$ decomposing into Sr_2ZrO_4 and $Sr_4Zr_3O_{10}$ at 1700°C. We note that this decomposition is not inconsistent with the incongruent melting of the composition $Sr_3Zr_2O_7$ observed[249] at 2250°C (equilibrium solid phase $SrZrO_3$), since those workers[249] did not observe the compound $Sr_4Zr_3O_{10}$. The stability of $Sr_3Zr_2O_7$ is not discussed[249], but it is pointed out that the diffraction pattern of a sample quenched from a melt of this composition does not contain lines of the compound $Sr_3Zr_2O_7$.

Since the tentative result of Ref. 256 appears to reconcile the inconsistency of the other data we take T_{tr} = 1700 ± 50°C as the recommended temperature for the decomposition of $Sr_3Zr_2O_7$ into $SrZrO_4$ and $Sr_4Zr_3O_{10}$.

8. Barium Zirconate

$BaZrO_3$. The congruent melting of $BaZrO_3$ has been demonstrated in a study[254] of the $BaO–ZrO_2$ system. From the published phase diagram[254] the melting point of $BaZrO_3$ is estimated as T_f = 2860°C. Circular 500,[9] referring to this work[254], gives T_f = 2700°C. By averaging these two estimates we arrive at the recommended value T_f = 2690 ± 20°C.

In 1976 Levitskii and coworkers[285] measured the high-temperature enthalpy of $BaZrO_3$ in the range 298–1606 K using a drop calorimeter. The normal temperature step of 80–120 K was decreased to 10–30 K in the region of the C_p anomaly. Temperatures of 758 ± 1 K and 1175 ± 1 K were obtained for the $\alpha \rightarrow \beta$ and $\beta \rightarrow \gamma$-$BaZrO_3$ polymorphic transformations. The experimental results are described by the expressions

Compound	Equation (cal mole^{-1})	Temperature, K
α-$BaZrO_3$	$H_T - H_{298} = 25.63\,T + 3.12 \cdot 10^{-3}T^2 + 2.82 \cdot 10^5/T - 8865$	298—758
β-$BaZrO_3$	$H_T - H_{298} = 27.77\,T + 0.09 \cdot 10^{-3}T^2 - 8272$	758—1175
γ-$BaZrO_3$	$H_T - H_{298} = 24.75\,T + 2.21 \cdot 10^{-3}T^2 - 7576$	1175—1606

Tentative values of the heats of these phase transitions, defined as the difference between the enthalpies of the two forms at $T = T_{tr}$, are quoted as $\Delta H_{758}(\alpha \rightarrow \beta) = 0$ and $\Delta H_{1175}(\beta \rightarrow \gamma) = 330$ cal mole^{-1}. The authors conclude[285] that the $\alpha \rightarrow \beta$ transformation is a phase transition of the second kind. We take the published[285] characteristics of these transitions as recommended values. The entropy of the $\beta \rightarrow \gamma$ transition is $\Delta S = 0.28$ cal mole^{-1} K^{-1}.

9. Strontium Hafnate

$SrHfO_3$. Berezhnoi and Belik[255] state that $SrHfO_3$ melts at 3163 K without mentioning the method of measurement. We take this as the recommended value, with an uncertainty of ±30 K.

Berezhnoi and coworkers[260] studied solid solutions of $SrZrO_3$ and $SrHfO_3$, and they calculated the heat and entropy of melting of $SrZrO_3$ from the phase diagram of the $SrO-ZrO_2$ system. They took $\Delta S_f = 5.5$ e.u. for the fusion of $SrHfO_3$ (equal to the value for $SrZrO_3$). Using their previous value[255] of T_f they calculated $\Delta H_f = 17.5$ kcal mole^{-1} for $SrHfO_3$. Assuming an error of ±1 e.u. in the estimate of ΔS_f we obtain an uncertainty of ±3 kcal mole^{-1} for ΔH_f. We propose these as the recommended values for ΔH_f, and 5.53 e.u. for the entropy of melting.

The high-temperature enthalpy of $SrHfO_3$ in the temperature range 675–2337 K was measured by Fomichev and coworkers[284] at 100 K intervals by the drop calorimetric method. Their results are described by the expression $H_T - H_{298} = 109.509T + 13.266 \times 10^{-3}T^2 - 1.260 \times 10^6/T - 27516$ (J mole^{-1}). No polymorphic transformations were observed in this work.

IV. ENTHALPY AND FREE ENERGY OF FORMATION

Kelley and coworkers[265] measured the enthalpy of formation of these compounds in a solution calorimeter (73.7°C, mixture of hydrochloric and hydrofluoric acid). Samples of mechanical mixtures of the oxides and of the compounds, contained in gelatin capsules, were introduced into the calorimeter at an initial temperature of 25°C. The heat of formation of the compound from its oxides at 25°C was obtained from the difference between the thermal effects accompanying the dissolution of the two samples. The thermochemical cycle for the hypothetical compound $MO \cdot TiO_2$, where M is an alkaline earth metal, is illustrated by the scheme

TiO_2 (cr.; 25°) + 4 H^+ (sol.; 73,7°) $\rightarrow$ Ti^{4+} (sol.; 73,7°) + $2H_2O$ (sol.; 73,7°) (ΔH_1)
MO (cr., 25°) + $2H^+$ (sol; 73,7°) $\rightarrow$ M^{2+} (sol.; 73,7°) + $2H_2O$ (sol.; 73,7°) (ΔH_2)
$MO \cdot TiO_2$ (cr., 25°) + $6H^+$ (sol.; 73,7°) $\rightarrow$ M^{2+} (sol.; 73,7°) + Ti^{4+} (sol.; 73,7°) + $3H_2O$ (sol.; 73,7°) (ΔH_3).

The heat of formation of $MO \cdot TiO_2$ from the oxides at 25°C is $\Delta H = \Delta H_1 + \Delta H_2 - \Delta H_3$. The composition of the acid mixture was 10.05 wt.% HCl + 10.05 wt.% HF. The experimental results were corrected for the heat of dissolution of the capsule in the acid. The error of the measurement of the heat of formation of the compound from the oxides was 0.3–0.5 kcal mole^{-1}.

Feodos'ev and coworkers used the method of combustion in a bomb calorimeter under standard conditions. A mixture of the alkaline earth carbonate MCO_3 and of the dioxide M_1O_2 (where M_1 = Ti, Zr, Hf) was pelleted with powdered graphite, used as an initiator in the proportion of 1 : 5. The reaction was

$$MCO_3 + M_1O_2 = MM_1O_3 + CO_2.$$

The heat of formation of MM_1O_3 from the elements was calculated by using the known heats of formation of the carbonates and of the oxides. The experimental results were corrected for the heat of formation of the nitric acid found among the combustion products, which were tested for completeness of the reaction and examined by X-ray diffraction. The unburned graphite was determined calorimetrically. The results for the titanates were in good agreement with those of Kelley and coworkers. The error of the measurements of heat of combustion was 0.3 to 0.8 kcal.

The original calorimetric results have been recalculated in this review by using the heats of formation of the oxides, carbonates, and CO_2 previously chosen during the compilation of Ref. 2.

1. Magnesium Titanates

$MgTiO_3$. Kelley and coworkers[265] obtained $\Delta H = -6.35 \pm 0.25$ kcal by solution calorimetry for the heat of formation of $MgTiO_3$ from MgO and TiO_2. Panfilov and Feodos'ev[266] measured in a bomb calorimeter the heat of combustion of air-dry MgO and TiO_2 mixed with graphite:

$$MgO \cdot x\,H_2O \cdot y\,CO_2 + TiO_2 = MgTiO_3 + x\,H_2O + y\,CO_2$$

and also the heat of combustion of MgO mixed with graphite:

$$MgO \cdot x\,H_2O \cdot y\,CO_2 = MgO + x\,H_2O + y\,CO_2.$$

Chemical and phase analyses of the combustion products were carried out[266]: the TiO_2 was determined as the insoluble residue after two extractions in boiling hydrochloric acid (1 h). The molar amounts of MgO and TiO_2 entering into the reaction were equal. $\Delta H = -5.5 \pm 0.1$ kcal was found[266] for the heat of formation of $MgTiO_3$ from the oxides. The discrepancy between the two results[265,266] exceeds the quoted experimental errors. In our choice of a recommended value we gave preference to Kelley's results[265], because they were obtained with a very pure sample of MgO (99.8%) containing small amounts of CaO, SiO_2, Fe_2O_3, and alkaline earths. The composition of the magnesium oxide used in Ref. 266 is more indeterminate. Using $\Delta H_f(MgO) = -143.76$ and $\Delta H_f(TiO_2$, rutile$) = -225.59$ kcal mole^{-1} we obtain $\Delta H_f(MgTiO_3) = -375.7$ kcal mole^{-1} from Kelley's result[265]. By combining this value with recommended entropy data we arrive at $\Delta G_f = -354.6$ kcal mole^{-1}. The error in ΔH_f and ΔG_f is less than 0.3 kcal mole^{-1}.

Mg_2TiO_4. The heat of formation of magnesium orthotitanate (spinel) from the oxides is given[265] as $\Delta H = -4.1 \pm 0.25$ kcal mole^{-1}. Using the heats of formation of the oxides assumed above we obtain $\Delta H_f = -517.2$ and $\Delta G_f = -493.8$ kcal mole^{-1} for Mg_2TiO_4, with an uncertainty not exceeding 0.5 kcal mole^{-1}.

$MgTi_2O_5$. Kelley[265] obtained $\Delta H = -4.45 \pm 0.25$ kcal mole^{-1} for the formation of the dititanate from the oxides. From this value we calculate $\Delta H_f = -599.2$ and $\Delta G_f = -566.2$ kcal mole^{-1} for $MgTi_2O_5$ by using the value $S(MgTi_2O_5) = 34.19$ e.u., or $\Delta G_f = -565.7$ kcal mole^{-1} by using the value $S(MgTi_2O_5) = 32.4$ e.u. (see Chapter II). The uncertainty in ΔH_f and ΔG_f is less than 0.7 kcal mole^{-1}.

2. Calcium Titanates

$CaTiO_3$. Kelley and coworkers[265] obtained $\Delta H = -19.35 \pm 0.25$ kcal for the reaction $CaO + TiO_2$(rutile) = $CaTiO_3$(perovskite). Panfilov and Feodos'ev[266] found $\Delta H = 22.5 \pm 0.2$ kcal for $CaCO_3 + TiO_2$(rutile) = $CaTiO_3 + CO_2$. The extent of the combustion reaction was 99%. Calculation from Kelley's result gives $\Delta H_f(CaTiO_3$, perovskite$) = -396.7$ kcal mole^{-1}, whereas from Ref. 266 we obtain $\Delta H_f = -397.6$ kcal mole^{-1}. The uncertainty of both values is ~0.5 kcal mole^{-1}. The value obtained by solution calorimetry is the more reliable because the reaction was quantitative, and we choose it as the recommended value. By combining this with entropy data we obtain $\Delta G_f = -376.3$ kcal mole^{-1}.

$\Delta G_f(CaTiO_3)$ data have been obtained by the e.m.f. method with a solid electrolyte. The e.m.f. of the cell O_2, Pt | CaO ‖ CaF_2 ‖ $CaTiO_3$, TiO_2 | Pt, O_2 has been measured[267] at 873 K. From the result we calculate $\Delta G_{298} = -19.11$ kcal for the potential-determining reaction $CaO + TiO_2 = CaTiO_3$, and $\Delta H = -18.86$ kcal, which gives $\Delta H_{f,298} = -396.2$ kcal mole^{-1}. E.m.f. measurements are reported also[268] for the galvanic cell Pt, $CaTiO_3$, CaO, $TiO_{0.5}$ ‖ $ThO_2 + La_2O_3$ ‖ M, MO, Pt, where M = Fe or Nb, in the range 1180–1290 K. From the results the authors calculated $\Delta H_f(CaTiO_3) = -398$ kcal mole^{-1} for the reaction $0.667CaO + 0.667TiO_{0.5} + MO = 0.667CaTiO_3 + M$ by using published values of the thermodynamic functions. This value is probably inaccurate because many data, covering a wide range of temperature, were used in the calculation.

Ca_2TiO_4. The functions ΔH_f and $S(Ca_2TiO_4)$ have been evaluated by the comparative calculation method[286]. The data used for the calculation are mutually inconsistent, and the work is of doubtful value.

$Ca_3Ti_2O_7$. Measurements[269] of the heat of dissolution of a mixture of oxides and of $Ca_3Ti_2O_7$ have given $\Delta H_f(Ca_3.Ti_2O_7) = -943.8$ kcal mole^{-1}. By using the chosen value of $S_{298}(Ca_3Ti_2O_7)$ we obtain $\Delta G_{f,298} = -896.1$ kcal mole^{-1}. The error in ΔH and ΔG is less than 1 kcal.

3. Strontium Titanates

We have previously reviewed[274] the thermodynamic properties of $SrTiO_3$, and chosen the values $\Delta H_{f,298} = -402.2$ kcal mole^{-1} and $\Delta G_{f,298} = -382.3$ kcal mole^{-1}, with an uncertainty not greater than 0.5 kcal mole^{-1}.

Sr_2TiO_4. Kelley[265] obtained -37.85 ± 0.25 kcal for $\Delta H_f(Sr_2TiO_4)$ from the oxides, which gives $\Delta H_{f,298}(Sr_2.TiO_4) = -552.2$ kcal mole^{-1}. Using $S_{298} = 38.0$ e.u. we arrive at $\Delta G_{f,298} = -524.6$ kcal mole^{-1}. The error in ΔH and ΔG is less than 2 kcal mole^{-1}.

4. Barium Titanates

The thermodynamic properties of $BaTiO_3$ have already been reviewed[274]. The values $\Delta H_{f,298} = -395.2$ kcal mole^{-1} and $\Delta G_{f,298} = -374.3$ kcal mole^{-1} were recommended, with an error of less than 0.5 kcal mole^{-1}.

Ba_2TiO_4. Kelley's value[265] of the heat of formation from the oxides is $\Delta H = -45.7 \pm 0.3$ kcal. Using the accepted values of ΔH_f for BaO and TiO_2 gives $\Delta H_{f,298}(Ba_2.TiO_4) = -533.3$ kcal mole^{-1} and $\Delta G_{f,298} = -507.0$ kcal mole^{-1}. The error is less than 2 kcal mole^{-1}.

$0.543BaTiO_3 \cdot 0.457SrTiO_3$. The same reference[265] gives $\Delta H_{f,298} = -397.9$ kcal mole^{-1} for this solid solution. Using the S_{298} value recommended here leads to $\Delta G_{f,298} = -377.7$ kcal mole^{-1}; the error of ΔH and ΔG is less than 2 kcal mole^{-1}.

$BaSrTiO_4$. The value -540.2 kcal mole^{-1} is recommended[265] for $\Delta H_{f,298}(BaSrTiO_4)$ from the elements. With the S_{298} value recommended here we obtain $\Delta G_{f,298} = -514.2$ kcal mole^{-1}, with an error not greater than 2 kcal mole^{-1}.

5. Calcium Zirconate

The function $\Delta H_f(CaZrO_3)$ has been determined[270] from the heat of combustion of a pelleted mixture of $CaCO_3$, ZrO_2, and graphite. An enthalpy change of $\Delta H = 35.2 \pm 0.2$ kcal was obtained for the reaction $CaCO_3 + ZrO_2 = CaZrO_3 + CO_2$, which took place in 85% yield. By combining this result with $\Delta H_f(CaCO_3) = -288.46$ kcal mole^{-1}, $\Delta H_f(CO_2) = -94.05$ kcal mole^{-1}, and $\Delta H_f(ZrO_2) = -263.04$ kcal mole^{-1} the value $\Delta H_f(CaZrO_3) = -422.3$ kcal mole^{-1} was obtained. The uncertainty, due mainly to the failure of the calorimetric reaction to go to completion, is less than 2 kcal mole^{-1}.

The heat of combustion of a mixture of CaO + Zr in a bomb under an oxygen pressure of 25 atm has been measured[287]. The value $\Delta H_f(CaZrO_3) = -400.3$ kcal mole^{-1} was obtained[287], and good agreement with the result of Ref. 270 (−398 kcal mole^{-1}) was claimed. However the value − 398 kcal mole^{-1} quoted in Ref. 270 is not ΔH_f but $\Delta G_f(CaZrO_3)$, and therefore the claim is groundless.

6. Strontium Zirconate

The function $\Delta H_f(SrZrO_3)$ has been determined[270] from the combustion of a mixture of $SrCO_3$, ZrO_2, and graphite (95% yield). The heat of this reaction was found to be $\Delta H = 38.2 \pm 0.2$ kcal. Using the value $\Delta H_{f,298}(SrCO_3) = -294.5$ kcal mole^{-1}, the standard enthalpy $\Delta H_{f,298}(SrZrO_3) = -425.3$ kcal mole^{-1} was calculated. Khekimov and coworkers[271] measured the e.m.f. of the galvanic cell O_2, Pt | SrO, SrF_2 ‖ CaF_2 ‖ $SrZrO_3$, ZrO_2, SrF_2 | Pt, O_2, in which the potential-determining reaction is $SrO + ZrO_2 = SrZrO_3$, in the temperature range 1180–1370 K. The heat of formation of $SrZrO_3$ from the oxides was calculated as $\Delta H = -18.6 \pm 1.5$ kcal, corresponding to $\Delta H_f(SrZrO_3) = -426$ kcal mole^{-1} (from the elements), in good agreement with the thermochemical value. However the thermodynamic functions of $SrZrO_3$ used in this calculation[271] were not the experimental values but estimated values, taken to be equal to the corresponding functions for $SrTiO_3$. Hence we shall ignore this result in choosing the recommended value of $\Delta H_f(SrZrO_3)$, and we give $\Delta H_{f,298} = -425.3$ kcal mole^{-1} and $\Delta G_{f,298} = -405.0$ kcal mole^{-1} for $SrZrO_3$, with an uncertainty of less than 1 kcal.

7. Barium Zirconate

The heat of the reaction $BaCO_3 + ZrO_2 = BaZrO_3 + CO_2$ has been measured[273] under the same conditions as the heat of combustion of $SrCO_3$. The result, combined with the accepted ΔH_f and entropy values of the oxides, leads to $\Delta H_{f,298} = -425.3 \pm 2$ kcal mole^{-1} and $\Delta G_{f,298} = -405.0 \pm 2$ kcal mole^{-1}. The heats of the reactions $Ba_3Al_2O_6 + 2ZrO_2 = BaAl_2O_4 + 2BaZrO_3$ and $ZrO_2 + BaF_2 + CaO = BaZrO_3 + CaF_2$ have been measured[288] by the e.m.f. method at 980–1120 K with a fluoride ion electrolyte. The calculated value[288] $\Delta H_f(BaZrO_3) = -423.4 \pm 2.6$ kcal mole^{-1} agrees very well with the thermochemical value.

The heats of formation of $CaHfO_3$ and $SrHfO_3$ have not been measured. Estimated values[289] of $\Delta H f$ for the hafnates, calculated by the equation $\Delta H_f(MHfO_3) = 1.001\ \Delta H_f(MSiO_3) - 34.2$ (kcal $mole^{-1}$), agree within 1% with the experimental value[272] in the case of $BaHfO_3$.

8. Barium Hafnate

The measured[272] heat of combustion of a mixture of $BaCO_3$, HfO_2, and graphite gave $\Delta H = 32.3 \pm 0.8$ kcal for the reaction $BaCO_3 + HfO_2 = BaHfO_3 + CO_2$ (97% yield). BaO was not detected among the reaction products, showing that $BaCO_3$ is stable under the conditions of the calorimetric experiment. The enthalpy $\Delta Hf_{,298}(BaHfO_3) = -431.5$ kcal $mole^{-1}$ is calculated from the result[272]. Taking $\Delta S_f(BaZrO_3) \simeq \Delta S_f(BaHfO_3) = -68$ e.u. for the formation from the elements we calculate $\Delta Gf_{,298}(BaHfO_3) = -411$ kcal $mole^{-1}$. The uncertainty of ΔH and ΔG is less than 2 kcal $mole^{-1}$.

The thermodynamic constants chosen in this review are summarised in Table 3.

Table 3. Recommended values of $\Delta H_{f,298}$, $\Delta G_{f,298}$, $H_{298} - H_0$, S_{298}, and $C_{p,298}$ for the alkaline-earth titanates, zirconates, and hafnates.

Compound	$\Delta H_{f,298}$, cal $mole^{-1}$	$\Delta G_{f,298}$, cal $mole^{-1}$	$H_{298}-H_0$, cal $mole^{-1}$	S_{298}, e.u.	$C_{p,298}$, cal $mole^{-1}$ K^{-1}
$MgTiO_3$	-375.7 ± 0.3	-354.6 ± 0.3	3240 ± 20	17.82 ± 10	21.96 ± 0.03
$MgTi_2O_5$	-599.2 ± 0.7	-566.2 ± 0.7	5360 ± 40	34.2	35.15 ± 0.05
$MgTi_2O_6$	—	-567.5	—	32.4	—
Mg_2TiO_4	-517.2 ± 0.5	-493.8 ± 0.5	4500 ± 30	27.5	30.76 ± 0.02
$CaTiO_3$	-396.7 ± 0.5	-376.3 ± 0.5	3800 ± 20	22.38 ± 0.10	23.34 ± 0.05
$Ca_3Ti_2O_7$	$-943\ 8\pm1$	-896.1 ± 1	9420 ± 70	56.1 ± 0.4	57.20 ± 0.05
$SrTiO_3$	-402.4 ± 0.5	-382.3 ± 0.5	4120 ± 40	26.0 ± 0.2	23.51 ± 0.02
Sr_2TiO_4	-552.2 ± 2	-524.6 ± 2	6060 ± 60	38.0 ± 0.3	34.34 ± 0.03
$BaTiO_3$	-395.2 ± 0.5	-374.3 ± 0.5	4230 ± 40	25.8 ± 0.2	24.49 ± 0.02
Ba_2TiO_4	-533.3 ± 2	-507.0 ± 2	6840 ± 60	47.0 ± 0.5	36.48 ± 0.10
$BaSrTiO_4$	-540.2 ± 2	-514.2 ± 2	6480 ± 60	45.8 ± 0.4	34.95 ± 0.10
$CaZrO_3$	-422.3 ± 2	-401.7 ± 2	3990 ± 40	23.9 ± 0.2	23.88 ± 0.02
$SrZrO_3$	-425.3 ± 1	-405.0 ± 1	4360 ± 40	27.5 ± 0.2	24.71 ± 0.02
$BaZrO_3$	-425.3 ± 2	-405.0 ± 2	4515 ± 40	29.8 ± 0.2	24.31 ± 0.02
$CaHfO_3$	—	—	—	25.9*	—
$SrHfO_5$	—	—	—	29.6*	—
$BaHfO_3$	-431.5 ± 2	-411 ± 2	—	31 8*	—
$Ba_{0,543}Sr_{0,457}TiO_3$	-397.9 ± 2	-377.7 ± 2	4210 ± 40	27.4 ± 0.2	23.38 ± 0.02

*Estimated.

V. DISCUSSION OF THE THERMODYNAMIC CHARACTERISTICS OF PEROVSKITES

The great majority of the compounds discussed here have the perovskite ABO_3 structure, where A is an alkaline earth element, and B is an element of the titanium subgroup. $MgTiO_3$ alone belongs to another structure type: ilmenite. All the other metatitanates are perovskites. According to Goldschmidt the transition from one structure to the other is determined by the tolerance factor $t = [R(A) + R(O)]\sqrt{2}[R(B) + R(O)]$, where $R(A)$, $R(B)$, and $R(O)$ are the ionic radii of the elements and of oxygen. Within the perovskite structure two types of co-ordination of the oxygen polyhedra are possible: the icosahedron, with a co-ordination number (c.n.) of 12, and the octahedron, with a c.n. of 6. The large ion of the alkaline earth element is surrounded by an icosahedron, the B^{4+} ion by an octahedron. The perovskite structure is stable for $0.8 < t < 1.0$, and for $t = 1$ it becomes ideal, with the closest contact between the A and B ions and the oxygen ions. For other values of t the ideal structure becomes distorted. The ilmenite structure, stable for $t < 0.8$, is characterised by an octahedral co-ordination of the O^{2-} ions around the cations. The case of $t < 1$ corresponds to free permutation of the type A cations in the co-ordination polyhedron, and the case of $t > 1$ corresponds to free permutation of the type B cations[277].

We shall examine the thermodynamics of the formation of an icosahedron (c.n. 12) around a large cation. There are compounds of the ABO_3 type which can exist in both polymorphic modifications (ilmenite and perovskite): for example, $CdTiO_3$. The energy relationships which determine the metal–oxygen bond in the octahedron and the icosahedron can be formulated. According to both theoretical and experimental crystal chemistry, compounds of a given type tend to have a definite metal–oxygen distance which is constant for a given c.n. It may be possible to calculate the energetics of the co-ordination polyhedra by using the heat of atomisation ΔH_a of the oxides $(MO_i)_c$ for the cases c.n. = 6 and c.n. = 12.

By definition, $\Delta H_a[(MO_i)_c] = \Delta H_a(M) + i/2D(O_2) - \Delta H_f[(MO_i)_c]$, where $\Delta H_a(M)$ is the heat of sublimation of the metal, $D(O_2)$ is the dissociation energy of O_2, and $\Delta H_f[(MO_i)_c]$ is the heat of formation of the oxide MO_i with a co-ordination number of 6 or 12. Consider the ratio $E_c = \Delta H_a[(MO_i)_c]/k$, where k is the co-ordination number, which characterises the energy of a single bond in the co-ordination polyhedron, and the quantity $A_c = E_c/R_c$, where R_c is the characteristic M–O distance in this polyhedron. It is convenient to express the thermochemical quantities in kcal, and the distances in Å. Characteristic distances are systematically reviewed in Ref. 275, and the thermochemical quantities are given in this review and in Ref. 2. In the oxides MgO, CaO, SrO, BaO, and CdO the cations under standard conditions are in an octahedral co-ordination of O^{2-} ions, with a c.n. of 6. In TiO_2(rutile) the Ti^{4+} ion also has a co-ordination number of 6, but Zr^{4+} and Hf^{4+} in their MO_2 compounds[276] have the very rare c.n. 7. When metatitanates are formed from the oxides the c.n. of M^{2+} can change, but the co-ordination polyhedron of Ti remains the same. When metazirconates and metahafnates are formed the oxygen polyhedra of both cations can change.

According to the published thermochemical data for Mg, Mn, Fe, Co, Ni, and Cd titanates the heat of formation of the ilmenites from their oxides is almost constant: $\Delta \overline{H} = -6 \pm 0.8$ kcal. In the case of $CdTiO_3$ we know ΔH_f for both the perovskite and the ilmenite modification: perovskite is the less stable by 3.6 kcal. The following thermochemical cycle can be used to evaluate the preference energy of the ion for the icosahedral co-ordination:

$$\begin{array}{l} (CdO)_{[6]} + TiO_2 = Cd_{[6]}TiO_3 - 6.6\ \text{kcal (ilmenite)} \\ (CdO)_{[6]} + TiO_2 = Cd_{[12]}TiO_3 - 3.0\ \text{kcal (perovskite)} \\ \hline (CdO)_{[6]}TiO_3 = (CdO)_{[12]}TiO_3 + 3.6\ \text{kcal} \end{array}$$

The subscripts [6] and [12] denote the c.n. of the Cd^{2+} ion. To this approximation the preference energy of Cd^{2+} for the icosahedral co-ordination is 3.6 kcal g-ion^{-1}.

The preference energy of the other ions can be estimated by assuming a ΔH_f of -6 kcal $mole^{-1}$ for the formation of the hypothetical ilmenite $ATiO_3$ from the oxides without change in the c.n. of the A ion, i.e. by taking the average of the heats of formation of the known ilmenites. With this assumption the preference energy of the ions for the icosahedral co-ordination of the perovskites is given by the expression $\epsilon = \Delta H_f + 6$ (kcal), where ΔH_f is the heat of formation from the oxides in the standard state. By using the ΔH_f values for the oxides and the titanates we obtain the following preference energies ϵ for some doubly charged cations:

Cation	Ca^{2+}	Sr^{2+}	Ba^{2+}	Cd^{2+}
ϵ, kcal g-ion^{-1}	—13.3	—26.4	—32.6	+3.6

From these ϵ values we can calculate $\Delta H_a(MO)_{12}$ in the hypothetical co-ordination with a c.n. of 12, and hence we can evaluate the quantity E_{12} which characterises the energy of a single M–O bond in the icosahedron and compare it with E_6 for the oxide in the standard state (Table 4).

Table 4. Heats of atomisation and energies of a single M–O bond in the octahedron and the icosahedron.

Cation in $MTiO_3$	ΔH_a $(MO)_6$ kcal mole^{-1}	ΔH_a $(MO)_{12}$, kcal mole^{-1}	E_6, kcal mole^{-1}	E_{12}, kcal mole^{-1}	A_6/A_{12}	R_{12}/R_6
Ca^{2+}	253.9	267.2	42.32	22.27	2.177	1.146
Sr^{2+}	243.0	269.4	40.50	22.45	1 997	1.107
Ba^{2+}	234.3	266.9	39.05	22.24	1.909	1.087

The transition of the alkaline-earth ion to the icosahedral configuration produces a remarkable levelling of the single-bond energy: the mean value is 22.32 ± 0.09 kcal per bond, i.e. within ±0.4%, as compared with a spread of 8% in the E_6 values.

The formation of Ca, Sr, and Ba metazirconates and metahafnates produces a change in the c.n. of both cations, and the heats of formation from the oxides are much lower than those for the corresponding titanates. This is evidently due to the expenditure of energy in transferring the Zr^{4+} and Hf^{4+} ions from polyhedra with a c.n. of 7 in the oxides to octahedra in the perovskites. Assuming a constant preference energy for the Ca^{2+}, Sr^{2+}, and Ba^{2+} ions to the icosahedral co-ordination from the original octahedra we can determine the energy of the transition of Zr^{4+} and Hf^{4+} to the octahedral co-ordination from the configuration with a c.n. of 7, which is characteristic of their dioxides. We assume that the heats of formation of the zirconates and hafnates from AO and the hypothetical oxide MO_2 with a c.n. of 6 are equal to the ΔH_f value of the corresponding titanates, which are formed without change in the c.n. of the B^{4+} ion. For $CaZrO_3$ (for example) we arrive at the following thermochemical cycle:

$$CaO + (ZrO_2)_{[6]} = CaZr_{[6]}O_3 \quad -19.3 \text{ kcal}$$

$$CaO + (ZrO_2)_{[7]} = CaZr_{[6]}O_3 \quad -7.5 \text{ kcal}$$

$$(ZrO_2)_{[7]} = (ZrO_2)_{[6]} \quad +11.8 \text{ kcal}$$

A similar calculation gives the energies of the transitions of the Zr^{4+} and Hf^{4+} ions in other compounds:

Cation in perovskite	Ca^{2+}	Sr^{2+}	Ba^{2+}
$\epsilon(Zr^{4+})$, kcal g-ion^{-1}	11.8	14.8	7.3
$\epsilon(Hf^{4+})$, kcal g-ion^{-1}	11.7	13.7	5.2

In spite of the significant difference between the $\epsilon(B^{4+})$ values, which is not surprising in view of the approximations made in the calculation, we think it legitimate to average these values, which gives $\epsilon(Zr^{4+}) = 11$ kcal g-ion^{-1} and $\epsilon(Hf^{4+}) = 10$ kcal g-ion^{-1} with a possible error of ±3 kcal g-ion^{-1}.

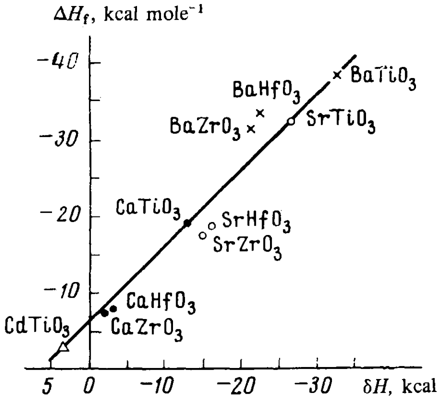

Figure 1. Heat of formation of perovskites from the oxides (ΔH_f) against energy of cation transitions (δH).

Table 5. Thermochemical and crystal chemical properties of perovskites.

Perovskite	ΔH_f, kcal mole^{-1}	ΔS_f, e.u.	t	Perovskite	ΔH_f, kcal mole^{-1}	ΔS_f, e.u.	t
	from the oxides				from the oxides		
$CaTiO_3$	—19.3	1.25	0.968	$SrHfO_3$	—18.7	—	0.938
$CaZrO_3$	—7.5	2.76	0.917	$BaTiO_3$	—38.6	—3.47	1.056
$CaHfO_3$	—7.7	—	0.922	$BaZrO_3$	—31.3	0.52	1.001
$SrTiO_3$	—32.4	0.72	0.985	$BaHfO_3$	—33.4	—	1.006
$SrZrO_3$	—17.6	2.21	0.934	$CdTiO_3$	3.6	1.75	0.954

Thus we may conclude that the heat of formation of the perovskite ABO_3 from the oxides depends on the energy of the cation transitions resulting from the change in the co-ordination of the oxygen ions surrounding the metal cation. The linear variation of ΔH_f with the quantity δ (the sum of the energies of the cation transitions accompanying the formation of the perovskite) is illustrated in Fig. 1.

In addition to the enthalpy of formation from the oxides, the entropy change is another important thermodynamic parameter of perovskites. ΔH_f, ΔS_f, and t values for a number of compounds are listed in Table 5. In most cases $t < 1$, denoting free ordering of the large cations in the icosahedra. The titanates should be treated separately from the zirconates, because there is no change in the c.n. of Ti (see Fig. 2). On going from $CaTiO_3$ ($t < 1$) to $BaTiO_3$ ($t < 1$) the ΔS_f value for the formation from the oxides changes sign and becomes negative. The tendency for the entropy of formation from the oxides to fall is found also in the zirconate group from $CaZrO_3$ to $BaZrO_3$. The stiffness of the M–O bond in the icosahedra increases as we approach the $t > 1$ region. This leads to greater ordering and to limited freedom of motion of large cation in the icosahedron, i.e. to a smaller entropy of formation from the oxides. In Ca, Sr, and Ba zirconates the freedom of the large cation increases from Ba to Ca, and the ΔS_f value increases in the same order. Although the entropy of the metahafnates of these elements has not been determined experimentally we can expect a similar behaviour. We should stress that the value of the tolerance factor t is strongly dependent on the choice of the system of ionic radii. We have chosen the system of Shannon and Prewitt[275], which is the most detailed and takes into account the spin state of the ion as well as the state of oxidation and the co-ordination number.

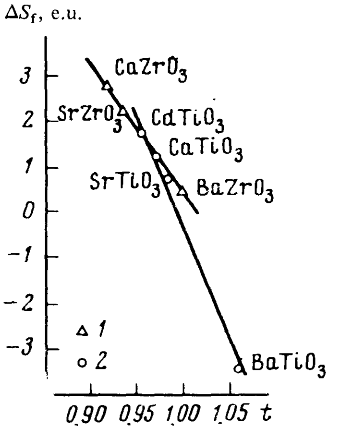

Figure 2. Entropy of formation of perovskites from the oxides (ΔS_f) against tolerance factor for (*1*) titanates and (*2*) zirconates.

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Molecular-kinetic Aspects of the Chemical Physics of the Condensed State

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Modern ideas on the elementary chemical step in condensed media are described in relation to reactions involving the transfer of energy, charge, a proton, and valence. It is emphasised that the rates of the above processes in solids and liquids are as a rule limited by the deficiency of free space and not of energy. Local fluctuations in entropy (the packing of the species), enabling the reactants to come into contact with one another in the correct coordination, assume particular importance because of this. The process is controlled either by the equilibrium density of such fluctuations or by the frequency of their generation, which is limited by molecular mobility.

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I. INTRODUCTION

The theory of the elementary chemical transformation in liquid and solid media is in an incomparably less satisfactory state than the theory of the elementary step in the gas phase. This is associated primarily with the fact that the mutual approach of the reacting species in the gas phase is described by the laws of mechanics, while in a dense medium their encounters take place in the course of random migrations in the solvent, i.e. are stochastic. However, the difference is not restricted to a difference in the kinematics of the encounters. Contact with the medium during the elementary step eliminates the energetic limitations which exist in the gas phase, but gives rise to steric hindrance in the reaction pathway associated with a deficiency of the free space required for the organisation of the reaction. Reaction rates in the condensed phase are frequently limited precisely by the amount of space liberated as a result of packing (entropy) fluctuations in the buffer environment surrounding the reacting species, and not in any way by the necessity to overcome energy barriers; the latter are known *a priori* to be not unduly high at a low temperature. Furthermore, when the ideas of gas-phase kinetics are formally applied to the condensed phase, the experimental activation energies are as a rule associated with definite energy barriers, even when they reach 3–4 eV, despite its being quite evident that barriers with this height are quite impossible to overcome. The causes of the very marked temperature dependence of the reaction rate constant should be sought not in the energetics of the elementary step, but in the type of molecular motion in the low-temperature condensed phase (diffusion, rotational mobility, viscous flow).

We shall consider initially the kinematic aspect of the problem and then the entropy-energetic aspect.

II. THEORY OF ENCOUNTERS

The rate constant for a bimolecular reaction occurring when the reacting species moving in a dense viscous medium encounter one another is defined by the expression

$$k = 4\pi R_e D, \tag{1}$$

where $R_e = R_e(D)$ is the effective radius of the encounter and D the diffusion coefficient. The gas-phase analogue of Eqn. (1) is the formula $k = \sigma v$, where $\sigma = \sigma(v)$ is the effective reaction cross-section and v the relative velocity of the colliding species. In a dense medium the diffusion coefficient is a measure of the rate of mutual approach and separation of the reacting species before the reaction (i.e. is an analogue of v). Accordingly, the $R_e(D)$ relation is the fundamental characteristic of the process mechanism. However, in contrast to $\sigma(v)$, this relation has been scarcely investigated owing to lack of an experimental method for the measurement of the diffusion coefficient.

Furthermore, the expected $R_e(D)$ relation is the same throughout according to the generally accepted point of view and is given by the formula[1]

$$R_e = R\frac{k_p}{k_p + 4\pi RD} = R\frac{k_p}{k_p + k_D}. \tag{2}$$

Both phenomenological parameters, namely the rate of reaction k_p during contact between the species and the distance R for which contact is established, are assumed to be constant and independent of the diffusion coefficient. The two-parameter Eqn. (2) constitutes the basis of the classification of reactions into kinetically and diffusion controlled. It is derived rigorously within the framework of the phenomenological "grey sphere" model, contact with which results in partial occurrence of the reaction[2]. The constancy of k_p and R is a consequence of the fact that the model rules out interaction at a distance and ignores its anisotropy and the role of motion at the instant of contact.

Furthermore, it became clear in the 1950s that this model is inapplicable to the description of reactions occurring over a considerable distance between the reactants. This happens, in particular, in the resonance transfer of electronic excitation in the long-range (dipole-dipole) interaction between the energy donor and acceptor. The interaction takes place over a distance amounting to several tens of Angstroms with the probability

$$W = a/r^6,$$

even if the distance r between the species remains unchanged during the reaction. However, the diffusion of species towards one another, which promotes their mutual approach, intensifies the energy transfer process, which is faster the smaller the value of r. In order to take into account this factor, Tunitskii and Bagdasar'yan[4] and a number of other workers[5,6] developed the theory of transfer at a distance accelerated by diffusion, and established that the flux of excited donors, directed towards the acceptor, is usually dissipated long before they come into direct contact (Fig. 1*a*). In this case Eqn. (1) includes the radius of the sphere within which all the donor excitations are quenched before the donors move away from their sites owing to diffusion and where all the excitations arising from outside are therefore destroyed. The more mobile the species, the closer they are able to approach one another before the energy transfer mechanism operates. For this reason, the effective radius of the quenching sphere

$$R_e = \frac{2\pi}{\Gamma^2(^1/_4)\sin(\pi/4)}\left(\frac{a}{D}\right)^{1/4} \tag{3}$$

decreases with increase of the rate of diffusion, although the reaction rate constant increases [see Eqn. (1)].

The picture of the process described above remains qualitatively valid also for any other interaction between the reactants, even in a short-range process such as the "exchange" interaction

$$W = W_0 e^{-2\varkappa(r-R_0)},$$

where κ^{-1} is the extent of the region of overlapping of the wave functions. In particular, such interaction is involved in the triplet–triplet energy transfer, which is forbidden by dipole factors[7]. However, it ensures electron transfer in glasses and frozen media over distances amounting to several molecular diameters[8-10]. In the absence of diffusion, these reactions are non-exponential, like the dipole–dipole energy transfer[11,12]. Only species present within the quenching zone, i.e. when $r \leqslant R_e$, react at this (static) stage. At a low concentration of the reactants, the fraction of such species is low, but the remaining reactive species are nevertheless destroyed owing to diffusion at a rate described by Eqn. (1), in which

$$R_e = R_0 + \frac{1}{2\varkappa}\left[\ln\frac{W_0}{4\varkappa^2 D} + 1.15\right], \tag{4}$$

as established by Fabrikant and Kotomin[13] and Doktorov and Burshtein[14].

The rates of both transport reactions described are limited by diffusion. However, Eqns. (3) and (4) contrast sharply with the constancy of $R_e = R = \text{const.}$, which follows from Eqn. (2) and corresponds to the usual hypothesis of diffusional control. A special investigation[15] showed that the "grey sphere" model is valid only when an extended interaction between the reactants can be replaced by a step with the equivalent thickness $R - R_0$ (Fig. 1*b*) and the latter must be small compared with the radius of closest approach R_0. Such a thin quenching layer is possible only in exchange quenching[15,16], but in this case too the step approximation $W(r)$ is possible only for a sufficiently high rate of diffusion: when $R_e(D)$ decreases to $R = R_0 + \frac{1}{2}\kappa$, Eqn. (4) is replaced by Eqn. (2), obtained for the "grey sphere" model[14]. On the other hand, if the reaction zone is insufficiently thin, agreement between the results of the distance and contact theories is achieved only at the kinetic stage (for a still higher rate of diffusion), and the phenomenological parameter

$$k_p = 4\pi\int_{R_0}^{\infty} W(r)\,r^2\,dr \tag{5}$$

acquires the significance of the total rate of reaction in the vicinity of the reaction centre.

Thus the distance theory not only includes the phenomenological contact model, but also imparts to it a microscopic significance. Furthermore, it describes the process also outside the limits of applicability of the contact model, when the rate of diffusion is very low. Despite these undoubted advantages, it is still very much inferior when compared with the theory of transfer reactions in the gas phase. The very fact that one begins with the locally defined probability $W(r)$ and not with the interaction Hamiltonian $\hat{H}(r)$ and a specific process mechanism demonstrates its inadequate microscopic significance. On the other hand, the very idea of transfer probability at any

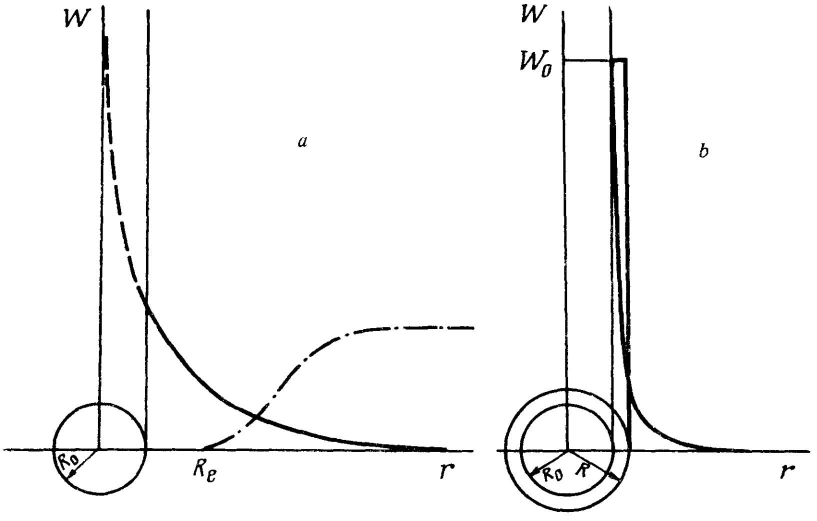

Figure 1. Dependence of the probability of quenching at a distance in dipole–dipole (*a*) and exchange (*b*) interactions on the distance between the reactants. The dash-dot line demonstrates how the stream of excited particles towards the sphere is dissipated in the presence of a strong long-range interaction.

point in space is specific to a condensed medium alone. In the gas phase one can only consider the results of the collision as a whole, but it is impossible to divide it into stages in an additive manner. The use of probabilities which are intrinsically additive becomes possible in condensed media, because any energy level E_i acquires a certain width Γ_i owing to the interaction with the solvent (Fig. 2). This restricts the free dynamic development of the transfer process to very short periods of the order of $(\Gamma_1 + \Gamma_2)^{-1} = \Gamma^{-1}$, after which the process begins to resemble to some extent α-decomposition occurring with the probability

$$W = \frac{2}{\hbar^2}\frac{b^2}{\Gamma_1+\Gamma_2},\ b = \langle 1|\hat{H}|2\rangle = b_0\,e^{-\varkappa(r-R_0)},$$

where $< 1|$ is the donor state, $|2 >$ is the acceptor state, and $E_1 \simeq E_2$. It is clear from this that the description of the transfer process throughout its extent in terms of probability is legitimate only when the encounters between the species during which the process takes place have a duration much longer than Γ^{-1}. Otherwise it is absolutely essential to generalise the theory in such a way that it permits a free dynamic development of the transfer process during the encounter.

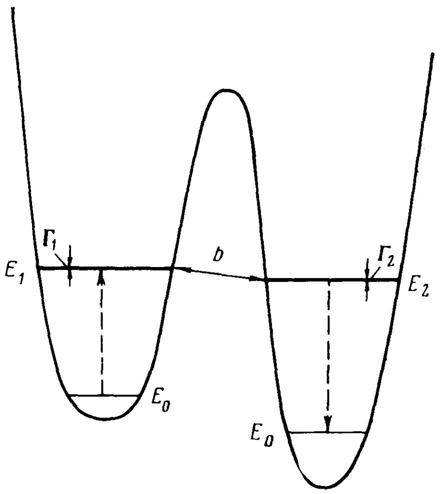

Figure 2. An energy scheme for the resonance transfer reaction. The dashed arrows indicate the excitation and deactivation of quasi-resonance levels.

Evidently the "encounter theory", which must satisfy this requirement, is not only kinematically more complex than the collision theory, but involves a greater number of parameters taking into account the interaction with the medium. The difficulties in devising this theory were overcome quite recently[14,16,17]. Formally, the apparatus of the theory describes resonance reactions in the liquid just as logically as in the gas. All the results of the distance theory were reproduced, and the limits of its applicability were established[14]. It was found that deviations from the "contact" formula (2) occur not only for slow diffusion, when it is overtaken by transfer at a distance, but also for extremely fast diffusion, which is able to switch the interaction on and off at a rate faster than the rate of relaxation[14]. In the latter case the interacting species can be regarded as just as free from interaction with the medium during the encounter as during the collision in the gas phase. The only difference is that the initiation and arrest of the interaction during the collision are predetermined in the course of free migration, while during the encounters between reactants in the liquid phase the occurrence of interaction is just as random as diffusion itself.

A general consequence of quantum mechanics is quadratic propagation in time of the resonance transfer process. At the dynamic stage, for very rapid diffusion, the probability of the reaction therefore depends quadratically on its duration τ_e, namely as $4b_0^2\tau_e^2/\hbar^2$, where $\tau_e = R_0/2\kappa D$. After multiplying by the frequency of encounters $(4\pi R_0 D)$, we obtain

$$k = \frac{4\pi R_0^3 b_0^2}{\hbar^2\varkappa^2 D}. \qquad (6)$$

This expression is the liquid-phase analogue of the Born approximation in the scattering theory. It follows from this that R_e diminishes quadratically as diffusion is accelerated:

$$R_e = \frac{R_0^3 b_0^2}{\hbar^2\varkappa^2 D^2}. \qquad (7)$$

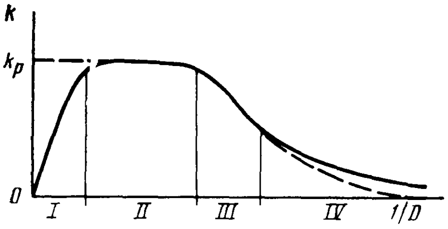

Figure 3. Dependence of the rate constant for a bimolecular reaction on the mutual diffusion coefficient: I) dynamic stage; II) kinetic stage; III) diffusion-controlled stage; IV) transfer over a long distance. The dashed curve illustrates the analogous relation obtained within the framework of the "grey sphere" model.

The qualitative deviations of the $R_e(D)$ or $k(D)$ relations (Fig. 3) from the generally accepted relations might become the subject of a special investigation if, together with the reaction rates, it was possible to measure molecular mobility. It is clear from the above formulae that this would make it possible to infer not only the type of interaction, but also its parameters, mechanism, and the "narrow" reaction stage. Unfortunately, the general kinetic standard procedure involves the measurement of the rate constant and at best its temperature dependence but never its dependence on D. This places liquid-phase kinetics in the same situation as that of its gas-phase analogue before the appearance of the molecular beam technique. No definite conclusions can be drawn about the intimate mechanism of the chemical reaction solely from the rate constant, while the choice of interaction parameters remains appreciably arbitrary.

Because of this, the theory continues to be extremely general. No other factors, apart from the charged state of the species[13,18,19], which hinders or promotes their mutual approach, are taken into account. Nevertheless, the interaction is almost always anisotropic. As a rule, the reaction centres occupy only a small section of the sphere associated with the molecule and rotational motion is an important factor, promoting contact between the reactants[20,21]. For example, this is the situation in spin exchange[22,23] and certain slow radical substitution reactions[24]. Furthermore, the reaction centre may be shielded by the solvation or hydration shell, the penetration of which (or residence in the latter) should limit the rate of the process in many instances. Finally, the presence of ligands in the reaction complex can both promote and hinder contact depending on the conformation, which should result in a direct dependence of the kinetically controlled reaction on the frequency of conformational transitions. It may be that, apart from the deviations from the contact model described above, caused by the unduly slow or unduly fast diffusion, there should be others associated with the fact that the molecule is not a sphere with a radius R and that contact with it is not simply of any type but must involve "adhesion" at the required site and in a convenient configuration. Although these claims are qualitatively evident, they have not been formulated in a strictly quantitative form, mainly because there is no possibility of comparing such a detailed theory with adequate experimental data.

III. REACTIONS CONTROLLED BY MOLECULAR MOBILITY

The transfer of an electron, proton, and valence in non-polar matrices does not as a rule require the overcoming of high potential barriers, and yet frequently shows an anomalously marked temperature dependence. We believe that this is evidence that the rate of diffusion of charge and valence is not limited by the height and extent of energy barriers but by the mobility of the matrix. Because of this, the observed rates of physicochemical processes are simply none other than the frequencies of molecular motions—vibrations, librations, and rotations, which have been the subject of acoustic and dielectric studies. Many specific examples discussed below support this claim.

Electron Transfer

In 1960 Tal'roze and Blyumenfel'd[25] observed a dark electrical conductivity $\sigma(T)$ in a large class of polymers with conjugated bonds. The anomaly was that activation energy for conduction in these substances varied from 0.2 to 4 eV, but the associated change in the pre-exponential factor (over the range of 60 orders of magnitude) fully compensated the changes in energy. In other words,

$$\sigma = \sigma_0 \exp(-E/k_B T),$$

but

$$\ln \sigma_0 = \alpha + \beta E, \tag{8}$$

where α and β are invariant in the given series of compounds (Fig. 4).

This phenomenon, called the compensation effect (CE), has been known in the physics of semiconductors since 1937 as the Meyer–Neidel effect[26,27], but it had been observed even earlier in chemical studies: in 1926 Constable[28] established that CE is characteristic of catalytic oxidation reactions and Roginskii and Rozenkevich found it in homogeneous unimolecular reactions[29]. After some controversy, Hinshelwood[30] recognised CE in 1947 as "one of the fundamental although incomprehensible relations of chemical kinetics", and subsequently Kobeko, who observed the effect in the most direct manner in styrene polymerisation reactions[31], concluded that "CE is a general law of chemical kinetics". In the 1960s CE was observed in the decomposition reactions of aliphatic azo-compounds and many hydroperoxides[32]. Furthermore, it was established that, in the reactions associated with alkaline hydrolysis[33], the compensation effect is to a large extent limited to an analogous compensation expressed by the temperature dependence of the solvent viscosity[34].

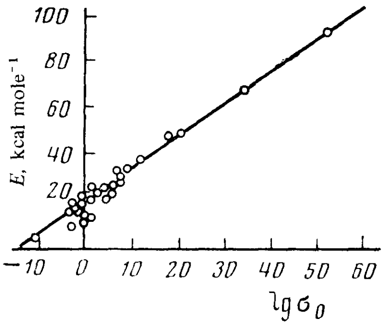

Figure 4. The compensation effect in the conductivities of a number of polymers according to Tal'roze and Blyumenfel'd[25].

The last observation might serve as the starting point for the interpretation of the effect in all its manifestations. However, there always remains the possibility that CE is associated with the very formulation of the experiment, the scope of which is frequently limited by the narrowness of the available temperature range. By a tendentious selection of specimens[35] or by postulating competition between two simultaneous reactions[36], it is easy to account for the compensation of the energy factor by the entropy factor if both are within reasonable limits. However, the CE observed in the electrical conductivity of organic structures[25] cannot for this reason be accounted for in a trivial manner, which gives rise to the problem of the origin of the exceptionally high activation energies appearing in the compensation series. Their occurrence in conduction in high-molecular-weight compounds was later confirmed for a large class of highly unsaturated polymers[37-39]. It is striking that the activation energy varies from specimen to specimen in a random manner, reaching 5 eV in certain cases. This phenomenon has been included as an experimental fact in monographs on organic semiconductors[40] and biopolymers[41], but a likely explanation for it has not so far been found.

The existence of activation energies exceeding all reasonable limits has been observed not only in electrical conduction, and not necessarily in the solid state. The activation energies for many catalytic processes[42] and a large class of liquid-phase enzymatic reactions, where CE is a universal phenomenon[43,44], are just as large. However, even if one admits that the phenomenon is non-trivial in a compensation series where the energies vary from several kcal mole^{-1} to 120 kcal mole^{-1} and more, one must treat with much caution many "simple" explanations of CE in series where the energy varies within reasonable limits. The widespread nature of the phenomenon makes it necessary to assume that its cause is extremely general and only its manifestations are not always anomalous (involving unduly large activation energies).

The appearance of activation energies of 4–5 eV is most paradoxical in electrical conduction, where the elementary step is particularly simple. The conductivity of the substance $\sigma = e\mu n$, where n is the concentration of current carriers and μ their mobility, is known to be linked to the diffusion coefficient by the Einstein relation:

$$\mu = \frac{eD}{k_BT}, \tag{9}$$

where e is the charge and T the temperature. In inorganic semiconductors the temperature relation $\sigma(T)$ is determined by the excitation of charges in the conductivity band, i.e. by the equilibrium current carrier density $n(T)$. However, a simple estimate shows that, when E = 2 eV, the forbidden gap is so wide ($2E$), that at room temperature there is not even one free carrier per specimen. In other words, in organic semiconductors with large values of E precisely the opposite situation should obtain: $n \simeq$ const., as in metals, and the temperature relation $\sigma(T)$ should originate mainly from the temperature dependence of the mobility of current carriers. The constancy of n can be explained by the fact that high-molecular-weight semiconductors contain a multiplicity of impurities, which need not necessarily be extraneous inclusions, consisting of low-molecular-weight oligomers with enhanced electron-donating or electron-accepting capacity, which ionise the main molecules. The current carriers thus generated move freely via the system of conjugated bonds within the molecule, experiencing difficulties only in the transfer from one molecule to another. If such transitions take place W times per second, their sum amounts to diffusion with the coefficient

$$D = \frac{a^2}{6}W, \tag{10}$$

where a is the scale of the spatial displacement of the current carrier in each elementary step of the intermolecular transfer (an analogue of the lattice period).

Taking into account Eqns. (9) and (10), it is reasonable to expect that the anomalous temperature relation $\sigma(T)$ is caused by the fact that the transition probability $W(T)$ is based on an activated process. However, until recently, it has been assumed that the electron independently traverses very large intermolecular distances, but not always "successfully" ($q \ll 1$[†]), repeating its attempts ν times per second from each end of the molecule. If this were so, it would be difficult to postulate any marked temperature dependence of the transition probability

$$W = \nu q. \tag{11}$$

In fact ν, the frequency of the intramolecular vibrations of the electron is constant, while the intermolecular transition is activated only when it takes place over a barrier. However, it is impossible to relate the observed activation energy to the height of this barrier. Even, for an attack frequency $\nu \simeq 10^{15}$ Hz, the transition through a 2 eV barrier would take place at a frequency of 10^{-7} Hz, i.e. only a few times per year.

The solution, pointed out by Gutmann as late as 1969,[45] is to abandon the usual treatment of charge migration as if the latter occurred in a frozen medium with a fixed geometry and positions of the molecules. In this approach, which is generally accepted in the theory of the solid state, the current carrier indeed has no choice but to overcome the barriers encountered in its path. In fact, there is always an alternative: either to pass through the barrier despite its considerable extent or to wait until it is lowered as a result of the mutual migration of molecules to such an extent that it becomes virtually "transparent". On the other hand, if the intermolecular distances are such that the barriers are on average insurmountable, only the latter possibility remains.

This is apparently the situation in organic semiconductors. The frequency of attempts ν in Eqn. (11) has the significance of the frequency of intermolecular contacts arising during thermal motion and not of the frequency of attacks (which is known to be high).

Table 1. Comparison of the activation energies for combustion and dielectric losses (measured in electron-volts).

Substance	$E_{\text{cond.}}$, eV	E_{loss}, eV
Chlorpromazine	1.5	1.4
Promethazine	1.5	1.37
Trifluoropyrazine	1.4	1.4
Poly(ethylene terephthalate)	1.65	0.66—0.87
Albumin	1.1	0.8
Polyacrylonitrile	0.85	0.61
Gelatin	1.5	1.14—1.3
Collagen	1.36	1.1

The probability of tunnelling at these instants $q \leq \frac{1}{2}$ can be very close to its limit ($\frac{1}{2}$) and the temperature dependence of conductivity, mobility, and the diffusion coefficient is then determined mainly by the temperature dependence of the frequency $\nu(T)$, which limits the rate of the process. Using these considerations, Gutmann decided to compare the measured activation energies for conduction and the dielectric losses, which constitute a direct means of measuring $\nu(T)$. The author notes that the "data compared proved to be very scanty because the objects investigated as dielectrics were as a rule not studied from the standpoint of their conductivity, and conversely".[45] Nevertheless he was able to make such a comparison (Table 1), partly on the basis of his own observations and partly on the basis of literature data, demonstrating the striking agreement of the results. The author explains the observed slightly higher activation energy for conduction (by 0.2 eV) by the necessary preliminary separation of the paired spins, which ensures the resonance mechanism of electron transfer. However, the main part of the activation energy and sometimes the entire activation energy is required solely for the creation of a "sterically convenient orientation of two molecules relative to one another, in which the energy barrier separating them is temporarily lowered".[45] In order to achieve this

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[†] Here q is the fraction of successful attempts.

favourable configuration, the molecules must bend, twist, or execute librations within narrow confines, and this stage actually limits the rate of the process. Electron transfer is merely an example of the reactions which may be controlled by molecular mobility, ensuring that the reactants come into contact in the required coordination.

Unfortunately, we have no data permitting a comparison of the activation energies for conduction and dielectric relaxation in the series of polymers where CE is observed. However, there is no doubt that such comparison would reveal their identity. The enormous activation energies and their consequent compensation by anomalously large pre-exponential factors in the expression for the rate of relaxation of dielectric losses in polymeric media are encountered extremely frequently[46].

Naturally, by reducing CE in electrical conduction to CE in molecular mobility, we do not as yet explain this phenomenon. However, the demonstration of the very fact that the reaction is controlled by molecular motion is important for chemical kinetics. Whether or not CE constitutes an unambiguous indication of such control can be elucidated only by a wide-scale comparison of the results of acoustic, dielectric, and molecular-kinetic investigations of condensed media with the rates of the elementary chemical reactions which occur in the latter. To what extent such a comparison can succeed is seen most clearly in relation to a simpler system, which we shall now analyse.

Proton Transfer

The anomalously high intrinsic conductivity of ammonium salt crystals, which is higher by 5–6 orders of magnitude than that of the corresponding alkali metal salts, constitutes an important reason for giving preference to the proton mechanism of charge transfer rather than to the usual vacancy mechanism associated with the motion of heavy masses. However, this hypothesis became concrete only recently as a result of a multistage experimental study of the formation and migration of a free proton in a crystal lattice[47,48]. In order to identify the mechanism, the proton-donating NH_4HSO_4 admixture was introduced by cocrystallisation from aqueous solution into $(NH_4)_2SO_4$ (AS), and $NH_4H_2PO_4$ (ADP) crystals; the concentration of the admixture was followed by titrating the solution after dissolving the given single crystal in water. As expected, the conductivity increased linearly with increasing concentration of the electron-donating molecules.

By following the concentrations in specimens with admixtures (n_0), it is possible to determine in the simplest way the proton mobility $\mu(T) = \sigma(T)/en_0$ and to compare its temperature variation

$$\mu(T) = \mu_0 \exp(-E_m/k_BT) \tag{12}$$

with the temperature variation of the intrinsic conductivity

$$\sigma(T) = e\mu(T)\cdot n(T) = \sigma_0 \exp(-E/k_BT),$$

where

$$n(T) = \sqrt{\frac{k_d}{k_r}[NH_4^+]} \propto \exp\left(-\frac{E_0}{2k_BT}\right) \tag{13}$$

is the equilibrium density of the protons generated as a result of thermal dissociation

$$NH_4^+ + SO_4^{2-} \underset{k_r}{\overset{k_d}{\rightleftarrows}} NH_3 + HSO_4^-$$

(k_d and k_r are the dissociation and recombination rate constants respectively). This comparison makes it possible to separate the contributions to the activation energy E by the dissociation energy E_0 and by the activation energy for motion E_m: $E = E_0/2 + E_m$. The values of E_0 and E_m proved to be virtually identical for protons in AS crystals: E_m = 0.49 eV and E_0 = 0.5 eV (E = 0.76 eV). However, although the origin of E_0 is evident, the nature of E_m still needs to be analysed.

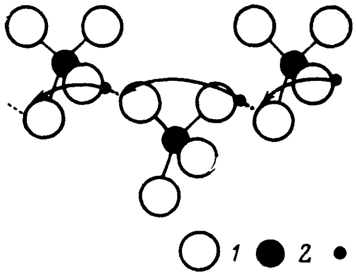

Figure 5. Schematic illustration of the multistage migration of a proton within and between the cells of the anionic sublattice: 1) oxygen atom; 2) sulphur atom; 3) proton. The arrows indicate the intraionic migrations of the proton and the circles illustrate the interionic migrations.

The migration of an intrinsic or impurity proton in the crystal lattice consists of elementary steps each of which is none other than a resonance transfer reaction of the type

$$HSO_4^- + SO_4^{2-} \underset{W}{\overset{W}{\rightleftarrows}} SO_4^{2-} + HSO_4^-. \tag{14}$$

The experimental mobility $\mu = (ea^2\gamma/k_BT)W$, where γ is the geometrical factor (instead of 1/6) taking into account the possibility of proton transfer to any of the anions forming part of the first coordination sphere, can be expressed in terms of the probability of this process W in accordance with Eqns. (9) and (10). Having measured μ, it is easy to calculate

$$W = \frac{\mu k_BT}{ea^2\gamma} = \nu q. \tag{15}$$

Evidently we encounter in Eqn. (15) the same alternative as in Eqn. (11). Although the probability W can be found readily, it is in no way clear to what the temperature dependence should be attributed: the probability of overcoming the barrier $q(T)$ separating the two anions or to the frequency of the approaches to the barrier $\nu(T)$. The latter is determined either by the rotation of the HSO_4^- ion or by proton transfer within the latter from one side to the other (Fig. 5). Rotation (a change in coordination) is a necessary condition for the translational motion of the charge carrier and it can be no less difficult than proton transfer along the line of the hydrogen bond between neighbouring lattice sites. In fact the distance between the sites in the tetragonal structure of the ADP crystal is 4.2 Å, while the distance traversed by the proton on moving from an oxygen atom of its "own" anion to a "foreign" anion does not exceed 0.35 Å. In this situation it is natural to suppose that the intramolecular transition may be the rate-limiting stage for the process as a whole.

Experimental proof of this was obtained by studying the temperature and frequency dependence of the complex dielectric constants of AS and ADP crystals. Direct measurements demonstrated the identity not only of the activation energies for conduction and dielectric relaxation, but also of the absolute values of the relaxation time τ_d and the rotation time $\tau_c = \nu^{-1}$ (Table 2) subject to the condition that $q = \frac{1}{2}$. The latter implies that whenever a favourable coordination is established the proton has sufficient time, while the coordination persists, to be equally distributed between neighbouring anions. The only difficulty is the creation of such a favourable situation and not the transfer step itself, which, judging from certain data[49], takes place at a frequency $\nu = 10^{13}$ s^{-1}, while the reorientation takes place, according to Table 2, at a frequency not greater than 10^6 times a second.

Table 2. Comparison of the activation energies and relaxation times for conduction and dielectric losses.

Ammonium salt	E_m, eV	E_d, eV	$10^5\tau_c$, s	$10^5\tau_d$, s
$(NH_4)_2SO_4$	0.49±0.03	0.51±0.04	3.3	5.5
$NH_4H_2PO_4$	0.54±0.03	0.50±0.04	8.3	4.6

Thus the seemingly elementary reaction (14) can be arbitrarily subdivided into two stages: the reorientation of the carrier anion

$$HSO_4^- \underset{\nu}{\overset{\nu}{\rightleftarrows}} SO_4H^-$$

and the intrinsic transfer (tunnelling) of a proton from one carrier to another:

$$SO_4H^- + SO_4^{2-} \underset{q}{\overset{q}{\rightleftarrows}} SO_4^{2-} + HSO_4^-,$$

the former being rate-limiting. This constitutes an example of a reaction controlled by molecular mobility in a pure form.

The ideas described apparently make it possible to consider the problem of the specific regulation of the rates of certain solid-phase protolytic reactions in a different way. Thus, on thermal decomposition, ammonium perchlorate (AP) initially dissociates:

$$NH_4ClO_4 \rightarrow NH_3 + HClO_4,$$

while the proton, having moved in the manner described above in the anionic AP sublattice, enters an unstable anion (ClO_4^- in the defective section of the lattice or as an impurity ClO_3^- anion) and destabilises it further, which leads to the initiation of the autocatalytic decomposition process. Consequently, by introducing additional protons into the AP lattice (from proton-donating additives) or by reducing the concentration of the conductivity protons present in the lattice (by introducing proton acceptors such as ammonia, HPO_4^{2-}, CO_3^{2-}, etc.), it is possible to decrease or increase correspondingly the thermal stability of this widely used solid-phase oxidant, which was recently demonstrated by direct experiments[50].

Recombination of Radicals

The thermal annealing of the radicals arising in a solid matrix under the influence of penetrating radiation has been the subject of chemical research in the course of two decades. After the discovery of the electron spin resonance method, these studies became particularly vigorous. However, despite the possibility of identifying radicals and of following their transformations, unambiguous and generally accepted explanations of the known anomalies in the kinetics of their recombination (pronounced departure from steady-state conditions, "shelves", etc.) have not so far been proposed. Virtually nothing is known about the mechanism of the spatial migration of radicals via molecular crystals, let alone glasses and polymers, and even diffusion coefficients have been measured only in exceptional instances. Nevertheless the mutual approach of radicals (or valences) in space constitutes a necessary preliminary stage before their recombination, which itself requires almost no activation energy. It is therefore natural to suppose that the rate of the process as a whole is as a rule limited by diffusion and that its temperature dependence and the CE frequently encountered in the process simply exhibit features characteristic of the temperature variation of the diffusion coefficient $D(T)$.

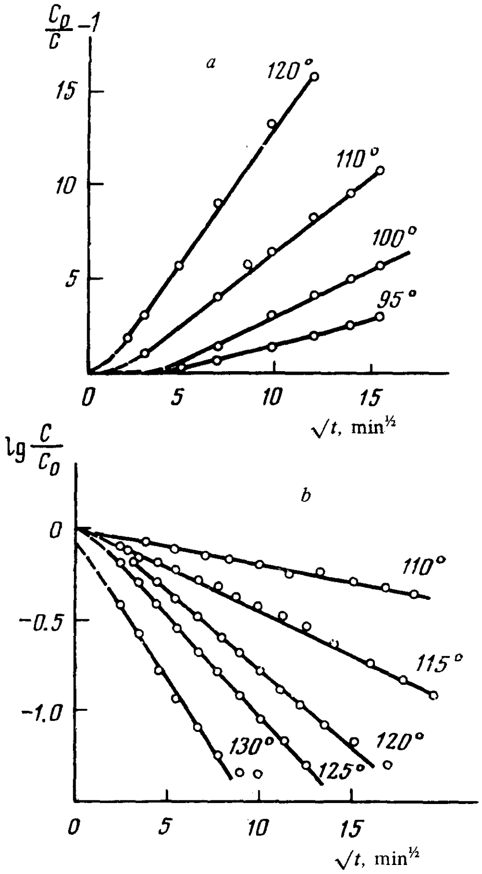

Figure 6. "Square root" plots designed to express in a linear form the kinetic curves for the unimolecular and bimolecular recombination of radicals in crystals of succinic (*a*) and 3,3-pentamethyleneglutaric (*b*) acids.

The present author and Tsvetkov[51] recently found direct evidence for this by observing that the kinetic curve for the unimolecular and bimolecular recombination reactions can be expressed in a linear form by plotting $\ln C$ and C^{-1} respectively against $\sqrt{t}$, whereas usually the variable plotted along the abscissa axis is t and not $\sqrt{t}$ (C is the concentration of radicals). The recombination in irradiated crystals of succinic and 3,3-pentamethyleneglutaric acids proceeds in this way at temperatures close to the melting point or the polymorphic transition temperature[51] (Fig. 6). Analogous "square root" kinetics had also been observed previously in vitreous matrices[52-55] and had been interpreted in the same spirit.

The decrease of concentration with increasing $\sqrt{t}$ always precedes the steady-state stage of the reaction, where it is controlled by diffusion ($k_p \gg k_D$) [see Eqn. (2)]. If after irradiation radicals are scattered throughout the bulk of the specimen randomly and uniformly and their motion in any direction takes place identically, then, according to the generally accepted theory[2], the rate constant for the diffusion-controlled reaction is

$$k_D(t) = 4\pi RD\left[1 + \frac{R}{\sqrt{\pi Dt}}\right]. \tag{16}$$

As in Eqn. (2), here R is the radius of the sphere which in this instance is "black". At the beginning of the annealing process the second term on the right-hand side of Eqn. (16) always predominates over the first and at this stage the recombination kinetics are therefore defined by the following equations:

$$(a)\ \frac{C_0}{C} - 1 = \tilde{k}\sqrt{t} \quad \text{or} \quad (b)\ \ln\frac{C}{C_0} = -\tilde{k}\sqrt{t}, \tag{17}$$

Indeed the $C(t)$ relation can be expressed in a linear form by means of the above "square root" plots and the effective reaction rate constant $\tilde{k}$ is

$$(a)\ \tilde{k} = 8R^2C_0\sqrt{\pi D} \quad \text{or} \quad (b)\ \tilde{k} = 8R^2M\sqrt{\pi D}, \tag{18}$$

where M is the concentration of the reactants involved in the first-order reaction. However, the non-steady stage, associated with the "square root" destruction of the species in direct proximity to the "black sphere", lasts only for an instant $t \ll R^2/\pi D$, i.e. for a very short time if R has molecular dimensions. During this period, only those few radicals which were generated along side one another or at a distance of one–two "steps" from one another can be destroyed. In fact a considerable proportion if not all the radical centres detected by ESR are destroyed in the non-steady stage of the reaction. Because of this, interpretation of the experimental data in terms of the above formulae yields for R a value many times greater than the size of the molecule or of the monomeric unit of the polymer: 40–80 Å. Such enormous capture radii can be accounted for solely by heterophase fluctuations in the prefusion region[56]: the appearance of unstable microscopic nuclei of the liquid phase within which the mobility of the species is very high. Two radicals which have entered such a "cauldron" have a greater chance of meeting and recombining, while a single radical simply moves in space, but over a considerable distance, of the order of magnitude of the fluctuation radius[51].

Unfortunately the situation remains paradoxical even if a hypothesis of this kind is adopted. When the radius of the black sphere, whose penetration leads to the inevitable destruction of radicals, is compared with the average distance between them at the beginning of annealing, the binary approximation within the framework of which Eqn. (16) was obtained ceases to be legitimate. Furthermore, certain kinetic curves indicate directly the internal inconsistency of their description in terms of this formula. This is clearly seen if the experimental results are expressed by a plot of $(C^{-1} - C_0^{-1})/t$ against $1/\sqrt{t}$; in this case Eqn. (16), describing the kinetics of bimolecular recombination, leads to a straight line[55], because

$$(C^{-1} - C_0^{-1})/t = 4\pi RD + 8R^2\sqrt{\frac{\pi D}{t}}. \tag{19}$$

The intercept which the line makes on the ordinate axis is none other than the steady-state rate of reaction (1). However, among the results quoted by Butyagin[55], there are also instances where the intercept is zero (Fig. 7, right-hand column); this involves the destruction of radicals in thermovulcanised rubber, where one can either assume that $R = \infty$ and $D = 0$, or that there is no steady-state stage in the reaction at all.

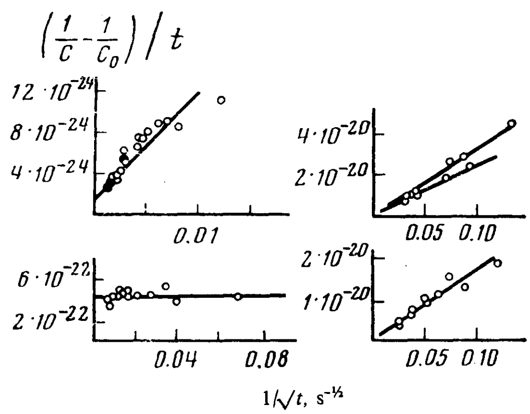

Figure 7. Kinetics of the destruction of radicals in the presence of a steady-state stage in the reaction (*a*) and in its absence (*b*) according to Butyagin[55].

The possibility of a non-steady-state course of the reaction from beginning to end merits special investigation. Such a possibility exists if diffusion takes place as a one-dimensional or two-dimensional process, but "square root" kinetics are obtained only in the one-dimensional case. The latter naturally arises if one of the radicals is always stabilised on the surface and the other in the bulk phase, or if both are formed at an edge dislocation consisting of a narrow (with a thickness of the order of magnitude of several atomic dimensions) tunnel in the crystal lattice. In order to ensure a markedly non-steady-state process, it is necessary to assume in addition that the initial distribution of radicals is very non-uniform. They must be generated close to one another compared with the distance by which they can be separated during diffusion. When the initial distribution is Gaussian with a width l, the destruction takes place in accordance with the law[57]

$$p = \frac{C}{C_0} = \frac{2}{\pi}\arctan\left(\frac{2}{l}\sqrt{\frac{Dt}{\pi}}\right), \tag{20}$$

if the radicals are assumed to be "black" and to recombine already in the first encounter.

The fundamental difference between Eqns. (20) and (19) is due to rejection of both fundamental assumptions of Waite's theory leading to Eqn. (16): the homogeneity of three-dimensional diffusion and the uniformity of the initial distribution of species. The process described by Eqn. (20) also consists of two stages; approximately half of the initial number of radicals are destroyed at each stage. However, the last stage is non-steady-state to the end and the recombination kinetics are close to the "square root" type whatever variables are used (Fig. 8). For any initial distribution $\varphi(x)$ (provided that it is narrow!), they can be represented in the following form:

$$\frac{C}{C_0}=\frac{l}{\sqrt{\pi D t}},\quad t\gg\frac{l^2}{D},\quad C\ll C_0, \tag{21}$$

where $l=\int\limits_0^\infty x\varphi(x)dx$ is the first moment of the distribution. Comparison of this destruction law with Eqn. (17a) readily shows that

$$\tilde{k}=\frac{\sqrt{\pi D}}{l}, \tag{22}$$

and $\tilde{k}$ therefore depends on the diffusion coefficient in exactly the same way as in Eqn. (18), although the values and significance of the spatial characteristics in the two formulae are different.

The above explanation of the profoundly non-steady-state nature of the process shows that at least the functional relation between the effective rate constants defined by Eqn. (18) and the diffusion coefficient can be accepted with confidence[‡]. This makes their comparison legitimate and their temperature dependence can be regarded as corresponding exclusively to the $D(T)$ relation. Although the constants for the two reactions investigated fit on the Arrhenius temperature relation $\tilde{k}=k_0\exp(-E/k_BT)$ and have similar values of $\tilde{k}$, the activation energies and the pre-exponential factors ($k_0=3\times10^{18}$ s$^{-1/2}$ and $E=36.4$ kcal mole^{-1} for 3,3-pentamethyleneglutaric acid, and $k_0=3\times10^{9}$ s$^{-1/2}$ and $E=18.4$ kcal mole^{-1} for succinic acid) differ from one another very markedly. Furthermore, a typical compensation effect due to diffusion is present. According to Eqn. (18), the activation energy for diffusion E_{q} is twice as large as the activation energy corresponding to the effective rate constant and reaches 3 eV for 3,3-pentamethyleneglutaric acid.

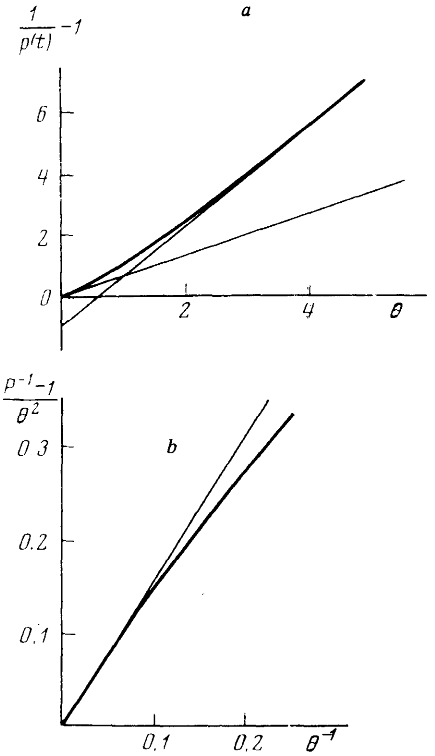

Figure 8. Kinetics of the non-steady-state recombination under the conditions of one-dimensional diffusion represented by plots in terms of the coordinates of Burshtein and Tsvetkov[51] (*a*) and Butyagin[55] (*b*); $p(t)=C/C_0$, $\theta=(2/l)\sqrt{Dt/\pi}$.

The compensation effect in the recombination of radicals had also been observed previously. It was interpreted phenomenologically as a result of the S-shaped pronounced $E(T)$ dependence, close to linearity[58]:

$$E(T)=E_0(1-\beta k_BT).$$

The steep decrease of the activation energy, which can explain the compensation effect in a narrow temperature range, was attributed to the unfreezing of the rotational mobility of the polymeric chain, i.e. not in any way "to the structure and properties of the radicals but to the structure of the polymer as a whole"[58]. Direct measurements performed on pure amorphous glycerol showed that the activation energies for the rotation (dielectric losses) and recombination of radicals are identical[59]. On the other hand, the non-Arrhenius S-shape of the relation between $\ln k$ and $1/T$ was later confirmed by a special study of recombination in irradiated frozen benzene[60] and was regarded by the authors as evidence in support of the hypothesis that the activation barrier to self diffusion (or the migration of valence) decreases with increase of temperature. Finally, direct experimental confirmation has

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[‡] Experimental evidence has become available quite recently, showing that the non-steady-state ("square root") kinetics are also characteristic of disproportionation reactions in the cage which do not require diffusion[80,81]. In particular[80], the reaction of the methyl radical with the matrix, $CH_3^{\cdot}+RH=CH_4+R^{\cdot}$, is markedly non-steady-state and proceeds in accordance with the law $C=C_0\exp(-\sqrt{kt})$. The difference between the rates of transformation of different radicals, which is the reason why the reaction is non-steady-state, may be attributed in this instance solely to the local inhomogeneity of the matrix, energetic or structural. The phenomenon has been interpreted[80] on the assumption that the transfer of H· has a tunnel and quasi-resonance mechanism and that the distribution of the resonance deficiency is Gaussian. The feasibility of this explanation of the "square root" decomposition shows that diffusion may not be the only cause of such behaviour and special proof is therefore required that it controls the process.

been obtained quite recently that the activation energies for recombination and diffusion in crystals are very close[61,62], i.e. that the nature of both phenomena is indeed the same.

IV. THE VACANCY MECHANISM OF MOBILITY

In view of the foregoing, it is natural to seek an explanation of the compensation effect outside the limits of chemical kinetics: in the mechanisms of the organisation of diffusion. However, the existence of a compensation effect is known reliably only for the diffusion of a number of metals into fused copper and for the self-diffusion of iron in its melts[63] (Fig. 9). Unfortunately the activation energies and pre-exponential factors in such cases vary outside the normal limits. On the other hand, in those instances where anomalies were encountered and were interpreted very successfully, the compensation effect had not been the subject of the investigation. We are dealing with extremely high (compared with potential barriers) activation energies and the correspondingly unduly high (by several orders of magnitude) pre-exponential factors in the expressions for the self-diffusion coefficients for atomic[64] and ionic crystals[65,66]. Despite the small scale of the effect, its explanation, which has withstood an experimental test, is the only reliable basis for considering the causes of the anomalously high activation energies and their compensation.

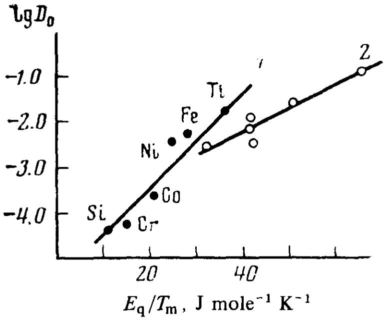

Figure 9. The compensation effect in the diffusion of metals in liquid copper (line *1*) and the self-diffusion of iron in Fe–C according to Shurygin and Shantarin[63] (curve *2*).

The migration of an atom (or ion) from its lattice site to a neighbouring site takes place most readily when the latter is vacant. Such a situation arises each time when the vacancy (Schottky defect) migrating in the crystal appears in the first coordination sphere. By treating such events as "encounters" between the vacancy and the ion, it is possible to determine their frequency by Eqn. (1), putting $R = a$ (a is the lattice constant), i.e. $W = 4\pi a D_V n_V$, where n_V is the equilibrium density of the vacancies and D_V is their diffusion coefficient. By migrating into a vacancy, the given species migrates over a distance $\sim a$, and the sequence of such migrations constitutes diffusion with the coefficient described by Eqn. (10), which in the given instance assumes the following form:

$$D = \gamma a^2 W = D_v P_v, \tag{23}$$

where $P_V \simeq a^3 n_V$ is the fraction of vacant sites in the crystal lattice. In this very familiar expression[65] D_V is a kinetic parameter and P_V a strictly equilibrium parameter. In principle, both depend on temperature, since the compensation effect in diffusion can originate both from kinetic and equilibrium causes.

Initially it was believed that the observed anomaly in the $D(T)$ relation is associated exclusively with the temperature relation $E_V(T)$ due to the barrier which the ion must overcome on being displaced into the nearest vacant site. The barrier between the sites is generated by the repulsion potential between neighbouring molecules and the ion must cross this barrier in order to enter the vacant site. The height of the barrier naturally depends on the distances between the sites. When the neighbouring molecules move apart as the crystal expands, liberating a pathway, the height of the barrier should decrease with temperature and the decrease should be linear:

$$E_v = E_0 + \frac{\mathrm{d}E_v}{\mathrm{d}v}\left(\frac{\partial v}{\partial T}\right)_p T = E_0[1 - \lambda r T], \tag{24}$$

where E_0 is the height of the barrier at $T = p = 0$, $\lambda = (1/v)(\partial v/\partial T)_p$ the isobaric coefficient of thermal expansion, $r = -\mathrm{d}\ln E_V/\mathrm{d}\ln v$ a numerical parameter, which can be readily estimated provided that the repulsion potential is known (the specific volume $v \simeq a^3$). For example, we have $r = 4$ for $E_V \simeq 1/a^{12} \simeq 1/v^4$. The linear decrease of $E(T)$, pointed out for the first time by Frenkel'[64], constitutes an excellent imitation of the Arrhenius relation and, by causing an unduly high activation energy, necessitates the compensation of such increase by the pre-exponential factor:

$$D_v = D_a e^{-E_v/k_B T} = D_a e^{\lambda r E_0/k_B} \cdot e^{-E_0/k_B T} = D_0 e^{-E_0/k_B T}. \tag{25}$$

However, when the compensation effect originates in this way, the activation energies can only be a little higher than the usual values $[(E - E_0)/E_0 \simeq \lambda r T \simeq 1]$ and the pre-exponential factor should not differ unduly from the true value. Even for ionic crystals, where the pre-exponential factor is too high by only four orders of magnitude, the kinetic compensation effect can account for only two orders of magnitude, i.e. for half of the observed effect. In this connection, Mott and Gurney[65] pointed out that the remaining half of the effect is evidently associated with the analogous effect as a function of $P_V(T)$. The increase of the density of vacancies with temperature is determined by the thermodynamics of the crystals and can be very marked near the melting point or the polymorphic transition temperature. A completely analogous situation occurs in pure metals and solid substitutional solutions where atoms diffuse via the vacancy mechanism[64]. The latter is regarded as involving local fusion due to a random aggregation of vacancies[67,68].

The kinetic and equilibrium compensation effects make equal contributions to the observed undue increase of the pre-exponential factor for ionic crystals, but whereas the former is interpreted at a microscopic level, the latter is introduced exclusively to make the theory consistent with experiment. The formula for the effect found empirically by Bugakov[69]

$$D = D_m e^{E/k_B T_m} e^{-E/k_B T}$$

is identical with Eqn. (8) and identifies $(\beta k_B)^{-1}$ with the melting point T_m. As the melting point is approached, the density of vacancies increases sharply and the probability of their binary, ternary, and higher-order collisions, leading to aggregation and microfusion, increases still more steeply, providing the driving force for diffusion and the reactions which it controls.

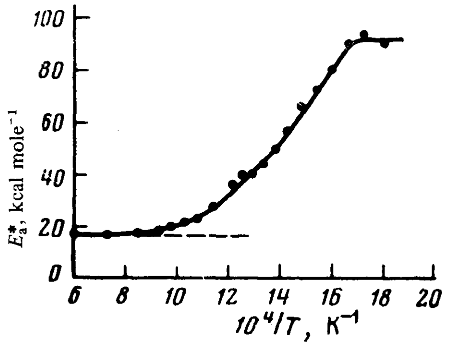

Figure 10. Dependence of the effective activation energy E_a^* for the viscous flow of the B_2O_3 glass over a wide temperature range.

In comparing the kinetic and equilibrium compensation effects as the possible causes of the appearance of anomalies of still greater magnitude, characteristic of molecular crystals and glasses, it is natural to give preference to the equilibrium effect. The fact that the temperature dependence of viscous flow and self-diffusion in such media has been attributed for a long time to the probability of the appearance of vacancies of molecular size v^* can be regarded as independent evidence in support of this choice. According to the free-volume theory[70,71], this probability is

$$P_v = \exp\left(-\frac{v^*}{v - v_0}\right), \qquad (26)$$

where v is the specific volume and v_0 is assumed equal to the intrinsic molecular volume (or the specific volume when $T = p = 0$). In the free volume theory the appearance of vacancies is attributed exclusively to entropy fluctuations; solely owing to the ordering of the structure and without an energy expenditure, such fluctuations lead to the accumulation of the free volume due to many molecules in one place, in the form of a cavity of specified size. Naturally, the greater the volume of this cavity v^*, the smaller the probability of its formation. On the other hand, the greater the average free volume per molecule $v - v_0$, the greater the frequency of cavities whose size is sufficient for spatial migration of the diffusing species in the latter. Consequently the isobaric temperature relation $P_V(T)$ is associated exclusively with thermal expansion. In vitreous matrices over a range of approximately 50°C near the glass point T_g the change in free volume is such that it converts Eqn. (26) into the so-called WLF formula[71,72] or Falcher's law:

$$P_v = \exp\left[-\frac{\text{const}}{T - T_0}\right], \quad T_0 < T_g. \qquad (27)$$

Despite its approximate nature, this law shows that the effective activation energy $(\partial \ln p_V/\partial T^{-1})_p$ increases rapidly with decrease of temperature and may be much greater than any potential barriers, as happens in the presence of the compensation effect.

Direct and precise measurements of the activation energy for low-temperature viscous flow and rotational relaxation in a reference glass such B_2O_3 showed[73] that the activation energy reaches 96 kcal mole^{-1} at low temperatures (Fig. 10). In the light of this finding, the appearance of an anomalous compensation effect in diffusion-controlled reactions such as recombination is quite natural.

Furthermore, since high activation energies and their compensation are characteristic of the rotational mobility of glasses, there is reason to expect that the compensation effect may be characteristic also of certain kinetically controlled reactions in glasses and liquids, which require contact between the reactants in the correct coordination. The stereospecificity of the reaction is expressed by the fact that its rate on contact between the reactants depends on the position of the point of contact on the reaction sphere of radius R:

$$k_p = k_p(\theta, \varphi),$$

where θ and φ are the angular coordinates of the point. In terms of the terminology of the model, this implies that the sphere is non-uniformly grey and, although there is a possibility of contact at any point with equal probabilities, owing to its different effectiveness, there is a multiplicity of different values of k_p, occurring with the probability

$$dW = f(k_p')\,dk_p'. \qquad (28)$$

Generally speaking, this distribution is diffuse compared with the model of a uniformly grey sphere, to which corresponds the distribution $f(k_p') = \delta(k_p' - k_p)$ or the model of a white sphere with grey spots, for which $f = (1 - q)(k_p') + q\delta(k_p' - k_p)$, where q is the steric factor equal to the relative area of the reactive surface. The relative rotation of the reactant simulates the rate of reaction during contact, and by virtue of this is capable of accelerating the process to some extent as a function of the form of $f(k_p')$. This implies that at the kinetic stage the process is controlled by rotational migration, the frequency ν of which may exhibit the same temperature dependence as the coefficient of translational diffusion. Griva and Denisov justly noted[28] that the proportionality $k = k_p \propto \nu$ (Fig. 11) "is a new phenomenon and is not predicted either by the theory of collisions in a liquid or by the activated complex theory". The authors explained this correlation on the hypothesis that, when it rotates, the molecule must overcome potential barriers generated by the environment. Orientation favourable for the reaction obtains in the vicinity of the maximum of one of the barriers. It is therefore reached only by molecules with sufficient rotational energy, the number of which is greater the faster the rotation. This view constitutes a modification of the activated complex theory in which an angular variable is the reaction coordinate[79].

However, the position favourable for reaction is not necessarily energetically unfavourable. If all the orientations are energetically equivalent, the rate of reaction is determined solely by its stereospecificity and by the mechanism of the reorientations and not in any way by the activation energy. This situation has been the subject of a special study for different models of chemical asymmetry under the conditions of jump reorientations by large and small angles in the cage. The rate of reaction over long periods, where it follows an exponential law, may depend on the frequency of the reorientations both linearly and in terms of the "square root" law ($\propto \sqrt{\nu}$).[74]

The dependence of the rate constant for the rotational or translational mobility of the reactant is a general feature of reactions controlled by molecular mobility, including those with kinetic limitations.

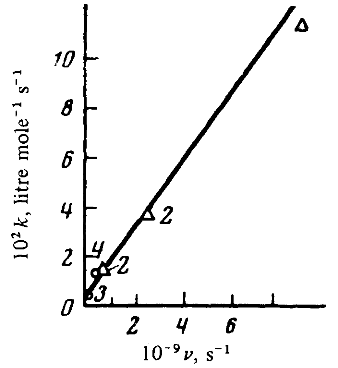

Figure 11. Direct proportionality between the rate constant for a liquid-phase reaction and the frequency of rotation of the reactant (a nitroxy-radical) at 22°C according to Griva and Denisov[24]: 1)–4) various solvents.

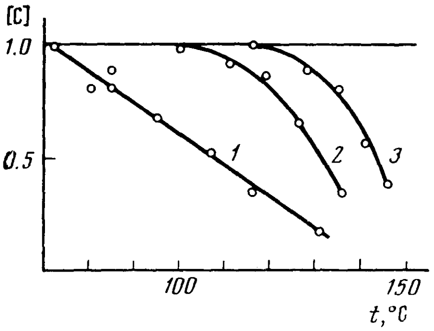

Figure 12. Curves for the annealing of radicals in crystalline adipic acid at different pressures: 1) 1 bar; 2) 2.8 kbar; 3) 4.15 kbar.

There exists a simple possibility of testing whether the process is activated and suffers from insufficient energy for its occurrence or from a deficiency of free space necessary for the organisation of the elementary migration step. The point is that $v = \text{const.}$ during isochoric heating and the probability defined by Eqn. (26) does not change as the temperature rises. This fact, namely the independence of the isochoric viscosity of simple liquids of temperature, has been used by Bachinskii as the basis of the free volume theory of viscosity[75]. Like Jost, having carried out isochoric measurements of diffusion coefficients in ionic crystals, he demonstrated very elegantly that the marked isobaric temperature relation $D(T)$, which is a consequence of thermal expansion, is abolished when the volume is fixed[66]. Assuming that the main factor in the recombination of radicals is the appearance of vacancies, which loosen the structure and facilitate the diffusion of species toward one another, the present author carried out an experiment involving the annealing of radicals in a high-pressure bomb, which makes it possible to prevent or hinder the expansion of the crystalline specimen during heating[76]. As expected, the recombination at the usual annealing temperatures did not occur at all, and the greater was the applied pressure, the higher was the rise in the heat treatment temperature necessary to achieve an appreciable transformation for a specified duration of heat treatment (Fig. 12).

Thus the only definite claim that can be made is that the compensation effect is associated with the steric difficulties in the organisation of the elementary step in a continuous medium. The liberation of space as a result of the aggregation of vacancies is more important than the accumulation of energy, which in any case cannot be used to achieve migration through a dense screen of molecules. Having been uniformly distributed in the first coordination sphere, the nearest neighbours create an impenetrable potential barrier and only fluctuations in their packing can create a breach in this wall. It is therefore not surprising that all investigators, whatever their concern (diffusion into metals[63], recombination of radicals[58-60], or solvation phenomena[77]), inevitably concluded that the compensation effect has a cooperative mechanism. The difficulties associated with the differentiation of the assembly of molecules involved in the elementary step, out of the total number present, constitute a problem which has not been solved theoretically and which is relatively unsusceptible to experimental investigation. However, progress in this field is necessary, since it is potentially capable not only of explaining the elementary step but also of leading to the discovery of means of controlling it.

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Even a simple change of emphasis, involving a change of attention from the energy to the entropy (packing) factor, is methodologically important for the chemical physics of the condensed state. The present author recently re-examined from this point of view the entire set of facts associated with the destruction of radicals generated by penetrating radiation in solid matrices[78]. It was found that the heterophase fluctuations associated with the transient local softening of the structure should lead in the first place (long before the unfreezing of diffusion) to the destruction of radical pairs and, increasing in scale with increasing temperature, should successfully "anneal" radicals increasingly remote from one other, which has been indicated by experimental data. When the fluctuations reach an extent sufficient not only for the establishment of contact but also for the spatial migration of the molecules, the static annealing of radical pairs gives way to diffusion-controlled destruction of randomly scattered radicals. Concepts of this kind might change from qualitative or semiquantitative ideas to rigorous constructions if the nature of molecular mobility did not have to be guessed at from indirect chemical data and could be inferred fairly definitely from direct physical measurements.

Unfortunately the chemical physics of condensed media has greatly outstripped molecular physics, and the lagging behind of the latter makes it virtually pointless to accumulate further uninterpreted data on the rate constants for elementary reactions in solid and liquid molecular media.

Nevertheless information about the structure of catalytically active centres, the complex, solvation, and hydration shells, the defective structures of crystals, and the short-range order in liquids, and especially the extension of the extremely scanty available information about molecular mobility in all such systems might sharply reduce the arbitrary features in the interpretation of chemical processes and permit a critical choice between the physical models of the elementary step.

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The Mechanism of the β-Elimination Reaction

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The latest studies on the mechanisms of the β-elimination reaction are considered and described systematically. The use of stereochemical and isotope effect data for the recognition of different types of reaction mechanisms is discussed.
The bibliography includes 232 references.

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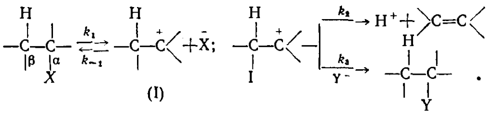
I. INTRODUCTION

Systematic research on the β-elimination mechanism began in 1927 when Ingold[1] attempted to investigate reactions of this type. Subsequently numerous studies devoted to the elucidation of the details of the mechanism were carried out[2-12]. All the mechanisms of the elimination reactions were divided into three classes[1-6]: *E*1, *E*2, and *E*1c*B*, in which the C−H bond is dissociated after, simultaneously with, or before the dissociation of the C−X bond respectively. There are also certain other less thoroughly investigated types of mechanisms.

II. THE *E*1 MECHANISM

1. General Characteristics of the β-Elimination Reaction via the *E*1 Mechanism

In 1935 Hughes[13] investigated a mechanism in which the slow stage is the ionisation of the initial reactant (substrate) preceding the rapid decomposition of the resulting carbonium ion. This unimolecular mechanism was called the *E*1 mechanism:


(1)

The carbonium ions (I) formed in the slow stage are subsequently consumed both in the elimination reaction and in nucleophilic substitution as a result of the interaction with the solvent molecules Y (or YH) or with other nucleophiles Y^- in the medium.

The occurrence of the reaction via the *E*1 mechanism is favoured by a molecular structure and media such that heterolysis of the C−X bond is faciliated[14]. In particular, the structural characteristics of the molecule, promoting the stabilisation of carbonium ions, play an important role[10,15]. For this reason, reactions via the *E*1 mechanism are more characteristic, for example, of tertiary, secondary, and α-aryl-substituted halides than of primary halides. Since the ability to carry a full positive charge is not characteristic of carbon atoms, stable carbonium ions have as a rule structures permitting extreme delocalisation of the positive charge[10,15]. The most important external factor, promoting a decrease of the positive ionic charge on carbon atoms, is solvation, because the vacant orbitals of the carbon atoms interact with the non-bonding electrons of the solvent molecules. Indeed, polar solvents promote the formation of carbonium ions and facilitate a reaction via the *E*1 mechanism, which competes in fairly strongly solvating but weakly nucleophilic media not only with the bimolecular *E*2 mechanism but also with the S_N1 mechanism. The elimination of toluene-*p*-sulphonic acid from *exo*-norbornyl toluene-*p*-sulphonate under the influence of a strong base in hydrocarbon solvents proceeds "purely" via the *E*2 mechanism. The same reaction in a tertiary alcohol involves predominantly the *E*1 mechanism[16]. The rates of the *E*1 reaction for menthyl and neomenthyl toluene-*p*-sulphonates in aprotic polar solvents vary in parallel with the dielectric constant of the solvent[17].

If the eliminated group X is an anion, its solvation by solvent molecules facilitates to a considerable degree the heterolysis of the C−X bond. In this case a smaller ion (for example Cl^-) will be solvated more effectively than a more diffuse ion (for example Br^-). When X is varied in the reactions of t-BuX in ethanol at 75°C, the ratio of the yield of the olefin to that of the substitution products increases in the sequence $\overset{+}{S}Me_2$ (0.18) < I (0.32) < Br (0.36) < Cl (0.44). When ethanol is replaced by acetic acid, the ratio changes in the same sequence, but to a more marked extent: from 0.12 for $\overset{+}{S}Me_2$ to 0.73 for Cl.[18] Since the solvation of anions is very important, weakly acid solvents (which interact with anions via hydrogen bonding) have a more ionising effect than basic solvents.

Since the carbonium ions formed as a result of the reversible heterolysis of the C−X bond can interact with the solvent, it is necessary that the β-hydrogen atoms should be split off rapidly. In the general case this last reaction stage has a low activation energy (~4 kcal mole^{-1}) and is highly exothermic; it is also favoured by the presence of substituents which are capable of being conjugated with the double bond formed.

If the rate of the carbonium ion formed in the slow stage of the reaction is decided in the subsequent rapid stages involving the elimination of a proton or interaction with the solvent, then the yield of the elimination product (as well as the ratio of the isomers if the latter are formed) should not depend on the nature of X for the given alkyl. Indeed this is approximately true for t-butyl, t-pentyl, s-octyl, and menthyl halides and the corresponding 'onium compounds in aqueous solvents[19]. In a series of t-butyl compounds whose ionisation potential varies by a factor of 900 the same relative yield of the olefin are obtained throughout the series with a variation of ±15%. Under these conditions, the carbonium ion decomposes immediately, although the counterion (leaving ion) is still very close; it is actually possible that the two ions form an unseparated ion pair. In media with high dielectric constants, such as nitromethane and acetonitrile, the ions acquire considerable freedom and even the above slight difference (15%) in the yields of the olefin vanishes.

Thus the *E*1 mechanism is preferred, provided that all or some of the following conditions are fulfilled: the presence at the α-carbon atom of substituents which may delocalise the positive charge on this atom and can become involved in conjugation with the double bond formed between the α- and β-carbon atoms; an enhanced capacity of the leaving group for ionisation; the presence of a highly solvating medium; the absence of a strong base which alters the mechanism to *E*2. All these conditions promote the heterolysis of the α-C–X bond without the simultaneous cleavage of the β-C–H bond.

2. Stereochemistry of Elimination Via the *E*1 Mechanism

As early as 1940, Hückel[20] showed that the stereochemistry of β-elimination depends on the reaction mechanism. Subsequently Hughes and Ingold[21] developed on the basis of stereochemical rules a theory of *E*1 and *E*2 reactions on which all subsequent studies of the stereochemistry of the elimination reaction are based.

The *E*1 reaction proceeds via a carbonium ion, the formation of which requires only the solvation of one carbon atom attached to the substituent, which is split off and the solvation of the substituent itself. The neighbouring carbon atom is not affected in this process. The second stage of the reaction, involving the elimination of a proton from a neighbouring carbon atom, does not impose special steric requirements, since the carbonium ion has a planar structure. For this reason, both *cis*- and *trans*- hydrogen atoms can participate in the *E*1 reaction. The relative amounts of olefins formed then frequently correspond to the thermodynamic stabilities, i.e. Zaitsev's [Saytzett's] rule holds. However, this rule cannot always be applied to elimination via the *E*1 mechanism, since in reality the situation is much more complex. The main aim of the examples quoted beflow is to give a general idea of the trend in research in this field.

The solvolysis of cyclopentyl derivatives proceeds at an unusually high rate (compared with acyclic and cyclohexyl analogues)[22,23], but in the majority of the published studies the yield of elimination products is not quoted. The studies by Hückel and coworkers[24], devoted to the alcoholysis of cyclopentyl toluene-*p*-sulphonate, permit the following conclusions: the reaction involves mainly the formation of ethers with a slight admixture of cyclopentenes; *cis*- and *trans*-2-alkylcyclopentyl toluene-*p*-sulphonates give rise to a large amount of cyclopentenes in which the Δ^1-isomer predominates; the *cis*-isomers react faster than the *trans*-isomers and gives a greater amount of the olefin. The stage determining the structure of the final product in these reactions is apparently the formation of an ion pair.

Analysis of the relative rates of solvolysis of isomeric monosubstituted cyclohexyl arenesulphonates is outside the scope of the present review, but it is discussed in detail in other reviews[22,23]. It is sufficient to say that the ratio of the rates of acetolysis, formolysis, and alcoholysis of axial 3- and 4-alkylcyclohexyl toluene-*p*-sulphonates to the rates of reaction of their equatorial analogues is of the order of 3.2–3.9.[25] The ratio of the rates involving the 3-substituted compounds does not differ greatly from the ratio of the rates for the conformationally similar 4-substituted analogues. The fact that the solvolysis of the axial toluene-*p*-sulphonate is faster may be attributed to the removal of steric hindrance on ionisation. This explanation presupposes that the two transition states for the ionisation of the axial and equatorial leaving groups can have different free energies, but the difference should be smaller than the difference between the free energies of the ground states. This approach appears to be quite reasonable[26].

The second factor responsible for the preferential ionisation of the axial leaving group compared with the equatorial group is that the positive charge formed is stabilised by the electronic interaction with the neighbouring β-C–H axial bond. This stabilisation can be regarded as a consequence of hyperconjugation or as a result of the involvement of the hydrogen atom in the stabilisation[27]. Whatever the nature of this stabilisation, it cannot be the decisive factor in the rate-limiting transition state in the formation of the cation as a result of the elimination of the equatorially oriented leaving group in the case of the chair conformation of the substrate, because the maximum effect requires the *trans*-orientation of the β-hydrogen and of the leaving group[26].

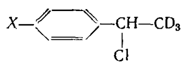
Examination of literature data[19,27–29] permits the conclusion that the *E*/*S*N ratio in the *E*1 reaction involving *cis*-2-alkylcyclohexyl derivatives is greater than for the *trans*-isomers, while *anti*-elimination yields exclusively the Δ^1-cyclohexene. The last effect is a consequence of the particular geometry of the six-membered ring (compared with the acyclic compound) and the greater stabilisation of the carbonium ion owing to the formation of a hydrogen bridge or hyperconjugation with the axial hydrogen atom in the β-position. As regards the *trans*-isomers, it appears that both *trans*-cyclohexyl and *trans*-4-t-butylcyclohexyl arenesulphonates are solvolysed, passing through the "twist" conformation in the transition state. The study of secondary isotope effects in the acetolysis of β-deuterated *trans*-4-t-butylcyclohexyl brosylates[27] and cyclohexyl toluene-*p*-sulphonates[30,31] as well as certain other data[32–34] lead to the same conclusion.

3. Isotope Effects in *E*1 Elimination

In principle, all three mechanisms of the β-elimination reaction can be distinguished by studying isotope effects[35]. More detailed differences within the limits of these broad classes can be effectively investigated by measuring the relative isotope effects for related compounds. Theoretical predictions and experimental findings obtained in the study of the isotope effects for the main types of mechanisms are given below. These predictions are qualitative and are based on the assumption that isotope substitution at the atom at which the type of bond is altered as a result of activation leads to an isotope effect (see, for example, Melander[36]). For more exact predictions, detailed calculations must be resorted to[37–40].

In the case of the *E*1 mechanism the primary isotope effect should be observed for a labelled group X and α-carbon [see scheme (1)], but not for labelled β-carbon and α- and β-hydrogens. Secondary isotope effects should be observed for α-hydrogens and for β-hydrogens not involved in the reaction. The carbonium ion (I) is a reactive intermediate species and appreciable β-carbon and α- or β-hydrogen isotope effects should not be observed in its decomposition[41]. If the reaction of (I) with Y has a high activation energy, then an isotope effect (slight or possibly even negative, since a bond is formed) should be observed when a labelled Y is used. The few available literature data on the isotope effect for a labelled group X are in the main consistent with the above predictions[42-49]. Numerous examples of α-hydrogen isotope effects in solvolytic and other substitution reactions have been published[50,51]. It has been shown that $E1-S_N1$ reactions have higher α-hydrogen isotope effects ($k^H/k^D = 1.15$ at 25°C) compared with the expected value, which corresponds to an appreciable weakening of the α-C–H bond in the activation process. One may assume that the elimination (or substitution) reactions in which α-hydrogen isotope effects differing markedly from the limiting values of the k^H/k^D ratio (at 25°C ~1.22 for X = F, ~1.55 for X = Cl, ~1.125 for X = Br, ~1.09 for X = I, and ~1.22 for X = OTs)[53] are manifested involve at least partially a mechanism different from $E1$ or S_N1.

The occurrence of a β-hydrogen isotope effect in $E1$ reactions has been demonstrated[51-57]. This can be accounted for by hyperconjugation—the delocalisation of sp^3-s electrons of the β-C–H bond over the α-p orbitals being formed. One might expect that the stabilisation by hyperconjugation of the positive charge generated on the α-carbon atom plays a smaller role when the positive charge is conjugated with a benzene ring, particularly one containing an electron-donating group, which thus leads to a decrease of the β-hydrogen isotope effect. The results of studies confirming this conclusion in relation to the solvolysis of 1-aryl-1-chloroethanes are listed below[51]:



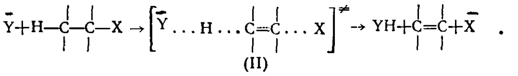
X	k^H/k^D
CH_3O	1.113
CH_3	1.200
H	1.224
NO_2	1.15
F	1.211

The standard value of the β-hydrogen isotope effect for the CH_3 group (data for t-butyl chloride[56]) is $k^H/k^D = 1.33$. All the values quoted above are significantly lower. The value for p-nitro-compounds is reduced compared with expectation owing to nucleophilic attack by the solvent on the α-carbon atom.

III. THE $E2$ MECHANISM

1. General Characteristics of β-Elimination Via the $E2$ Mechanism

The $E2$ mechanism is the commonest of all the elimination mechanisms and can be represented by the following scheme:



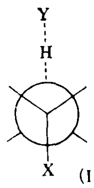
$$\bar{Y}+H-\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}-X \rightarrow \left[\bar{Y}\ldots H\ldots \overset{|}{\underset{|}{C}}=\overset{|}{\underset{|}{C}}\ldots X\right]^{\neq} \rightarrow YH+\overset{|}{\underset{|}{C}}=\overset{|}{\underset{|}{C}}+\bar{X} \quad (2)$$

(II)

According to this scheme, the reactant Y, called the base, removes a proton from the β-carbon atom of the substrate and the electron-accepting leaving group X is synchronously separated from the α-carbon atom. This mechanism does not involve any intermediate stages and thus has only one transition state between the reactants and the products. The reaction is of second order overall—of first order with respect to each reactant.

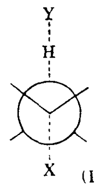
In his early studies Ingold[1] already pointed out that it is not obligatory that the dissociation and formation of bonds in an $E2$ reaction should occur absolutely synchronously; in 1956 Cram et al.[58] established that the structure of the transition state in $E2$ reactions may be different for different substrates under identical reaction conditions and may vary for the same substrate when the reaction conditions are altered. It has now been demonstrated that in reality there is a whole set of $E2$ mechanisms with different transition states[2,3,59,60] whose structure may vary smoothly with that of the substrate and the reaction conditions; these variations are limited on either side by extreme cases—$E1$-like and $E1cB$-like transition states—and do not extend beyond the region where true carbonium ions and carbanions exist. The mechanism is believed to be synchronous ($E2$) when a base is involved in the transition state, but there is no exchange of hydrogen atoms.

It is very important to emphasise that the type of the transition state is not a constant property of the substrate, but depends also on the nature of the solvent and the base. In such cases the predictions and interpretation of the experiments frequently become arbitrary and it is usually more correct to refer the reaction to a particular special case and to a specific type. Four main types of the transition states in $E2$ reactions are given below:



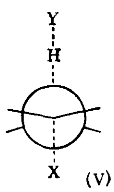
(III)

$E1cB$-like



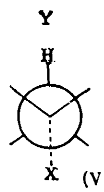
(IV)

Synchronous reactant-like



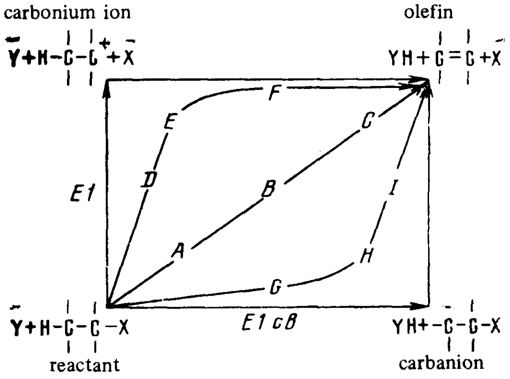
(V)

Synchronous olefin-like



(VI)

$E1$-like



Schematic illustration of the changes in the transition state in the elimination reaction (various types of the $E2$ mechanism).

A new method for the representation of a variety of transition states for $E2$ mechanisms, which proved to be the clearest and most convenient, was proposed recently[61]. The Figure represents schematically various $E2$ mechanisms on the basis of the potential energy surface diagram. Each section, denoted by a letter within the limits of the diagram, corresponds to a definite type of activated complex with its own potential energy surface; the positions of these sections relative to the species designated in the corners of the diagram indicate the structural characteristics of the various activated complexes and their positions on the reaction coordinate.

For example, the activated complex *A* is reactant-like (with a slight weakening of the β-C–H and α-C–X bonds and a slight double-bond character of the α-C–β-C linkage). According to Hammond's postulate[62], this activated complex may be formed in reactions giving rise to a very stable olefin.

The activated complex *F* is "carbonium ion- and olefin-like" with a significant weakening of the α-C–X bond, an appreciable double-bond character of the α-C–β-C linkage, and considerable transfer of a hydrogen atom from β-C to the base. Section *B* describes the "central" synchronous transition state. Thus the transition state in an *E*2 reaction can occupy any point within the given diagram, without going outside its limits.

The relations between the factors influencing the structure of the transition state are very complex, but the predictions described below appear to be well-founded and agree with the experimental data which will be examined subsequently.

Type (III) (the *H* region in the Figure) is favourable for compounds in which the β-hydrogen atom is labile owing to the inductive *–I* effect of α- or β-substituents; the rate of reactions proceeding via such an activated complex will be appreciably influenced by factors determining the acidity of the β-hydrogen. Such reactions are particularly facilitated in the presence of substituents delocalising the negative charge owing to conjugation or of substituents with *cis*-steric effects (see above). The use of strong bases as well as solvents which do not favour the ionisation of groups eliminated from the α-position also favours the occurrence of reactions with an *E*1*cB*-like mechanism.

The "*E*1-like" type (VI) (the *E* region in the Figure) is favoured by factors such as the presence of electron-donating substituents, which increase the electron density at the α-carbon atom, steric effects, and solvents favouring the extension of the C–X bond. The strength of the bases and the polar and steric effects of β-substituents have little importance in this instance, but the α-substituent, which delocalises the positive charge owing to conjugation, should influence the reaction rate.

Evidently types (IV) and (V) (*E*2 synchronous types; *A* and *C* regions in the Figure) have the characteristics of types (III) and (VI), but exhibit a specific sensitivity to α- and β-substituents and a high β-hydrogen isotope effect. In such cases bulky α- and β-substituents give rise to a pronounced *cis*-effect, since the double bond in the activated complex is fairly well formed, but small substituents may favour this type of transition state as a result of conjugation.

The influence of various factors on the structure of the transition state and the rate of *E*2 reactions has been examined in a number of reviews[3–12], from which it follows that in general low concentrations of the base favour unimolecular reactions (*E*1, S_N1). On the other hand, at a high concentration of the base, bimolecular reactions predominate (*E*2, S_N2), the relative contributions of which depend both on the structure of the substrate and on the ratio of the basicity of the base employed (attack on H) to its nucleophilic strength (attack on C).

Another approach is based on the hypothesis that the rate of *E*2 reactions depends in this instance on the H_- function at a high concentration of the base if there is a vigorous transfer of the proton to the base in the transition state[63]. The ratios of the rates of the base-catalysed elimination for para-substituted β-chloroethyl phenyl sulphones in anhydrous acetonitrile when Et_3N, $Et_2NCH_2.CH_2OH$, $EtN(CH_2CH_2OH)_2$, and $N(CH_2CH_2OH)_3$ are used as bases are 550 : 52 : 6.6 : 1 respectively[64]. This shows that the rate of reaction is correlated with the basicity of the bases. The Hammett reaction constants ρ for these reactions are respectively 1.81, 1.75, 1.72, and 1.64. Such variation of the reaction constant shows that the carbanionic character of the transition state becomes more pronounced with increasing base strength, moving into the *H* region (see Figure). Other investigators[65–67] arrived at the same result in studies of the influence of the base strength on the ratio of the yields of the products of *E*1, S_N1, *E*2, and S_N2 reactions and on the yield of isomeric olefins from various substrates. However, this type of correlation is not always observed[68–70]. The study of nine reactions in a concentrated NaOMe solution showed[71] that there is no direct correlation between the rates of reaction and the H_- acidity functions or the stoichiometric concentrations of the base.

The breakdown of the linearity in the relation between the rates of *E*2 elimination and base strength can be due to the smooth variation of the structure of the transition state[58] as the base strength is altered, which may lead to a change in mechanism. For this reason, in a study of the influence of the basicity of the medium both on the rate and the mechanism of the reaction, it is desirable not to confine the investigation to the measurement of the reaction rates alone and to determine also other characteristic reaction parameters (such as the reaction constant and the isotope effect) in order to be able to arrive at more clear-cut conclusions on comparing these parameters.

Such a combined study of the elimination of HBr from 2-arylethyl bromides in the t-BuOK–t-BuOH system has been carried out by Saunders and coworkers[72]. They investigated the influence of the addition of dimethyl sulphoxide (DMSO) on the rate, the isotope effect, the reaction constant, and the activation parameters of the above reaction. We observed that the addition of DMSO causes an unusually marked acceleration of the reaction (by a factor of 12 at 30°C for a 0.965 M DMSO solution and by a factor of 120 for the 2.23 M solution). Despite the fact that DMSO has a much higher dielectric constant than t-butyl alcohol, the value of *E* (and *Z*) for these solvents are almost identical[73]. Consequently there can be no great difference between their solvating capacities in relation to a neutral alkyl bromide and a transition state with a delocalised charge. Thus the acceleration could have been caused only by a change in the basicity of the t-butoxide. However, with increase of the DMSO concentration from 0.965 to 2.23 M, the rate of elimination for 2-phenylethyl bromide increases by a factor of 10, while the basicity changes only slightly (only by a factor of 1.5). The authors[74] believe that the usual basicities, determined experimentally, are unsuitable for the consideration of the influence of "basicity" on the structure of the transition state in the reaction. It was shown[74] that the base strength and the type of solvent are more important factors than the size of the base and the direction of its approach to the reagent. The association of the catalyst[75] as well as ion–dipole and ion–ion interactions between the base and the leaving group[76] play a particularly important role.

The idea that the hydrogen bonding and hence the "levelling effect" of protic solvents may influence the basicity of oxygen-containing anions was tested experimentally 35 years ago[77]. Furthermore, the polarity of the transition state in an $E2$ reaction is usually lower than that of the initial state, since the ionic charge of the base is distributed over a larger area. For this reason, polar solvents should reduce the reaction rate. Since the charge in the transition state of the elimination reaction is more delocalised, the decrease of the rate is in this case manifested to a greater extent than in the corresponding substitution reaction (S_N2), which frequently accompanies bimolecular elimination reactions[78,79].

There is no need to consider in detail each individual investigation in the present instance, but one must note that studies in recent years have been largely devoted to an experimental test of the above considerations. They showed that both variation in base strength and solvent polarity[80-82] and changes in the structure of the substrate[83-86] influences the rate of elimination[87,88] and lead to a change in the structure of the transition state, as a result of which it may occupy an infinity of positions on the potential energy surface between the limiting "$E1cB$-like" and "$E1$-like" types[89].

2. Stereochemistry of the Elimination Reaction Via the $E2$ Mechanism

Until recently[90] the stereochemical characteristics of $E2$ reactions were thought to be determined by Ingold's four-centre rule, which states that bimolecular elimination proceeds smoothly only when the four centres involved in the reaction lie in the same plane, i.e. when the substituents being eliminated are in the transoid conformation (in the *anti*-position relative to one another) or in an eclipsed cisoid conformation. For rigid cyclic systems, an analogous rule was formulated by Barton, while the steric limitations in elimination reactions involving bridged rings are determined by Bredt's rule.

However, the current views on the stereochemistry of the $E2$ reaction have altered radically; it has been established that, for *cis*-coplanar leaving groups, the $E2$ reaction proceeds just as fast as in the case where the groups are *anti*-periplanar and that *cis*-$E2$ elimination cannot be ruled out either in acyclic or cyclic systems.

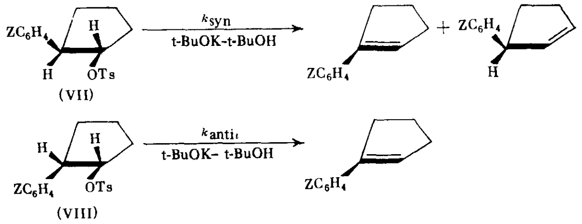
Furthermore, β-elimination reactions have been achieved with bridge compounds despite being "forbidden" by Bredt's rule. These problems are discussed in special reviews[25,91-96]. It is important to note that both the bulk of the base and of the leaving group and the degree of branching of the substrate molecule play a role in the alteration of the relative contributions of *cis*- and *trans*-elimination reactions[94,97-99]. Analysis of the proportions of the products of elimination from PhCHDCHDX (X = p-$MeC_6H_4SO_3$ or Cl) using t-BuOK in t-BuOH, DMSO, or benzene showed[100] that *syn*-elimination takes place only in benzene and that *syn*- and *anti*-elimination reactions lead to different primary hydrogen isotope effects. The above study gives an idea of the important role in *syn*-elimination of the ion pair formed by the base.

The latest studies on the general aspects of the stereochemistry of this reaction[101] as well as *syn*-elimination[102-104] again confirmed the influence of the formation of the ion pair on the stereochemistry of the process[105] and also the important role of the base and the solvent[106]. After it was discovered that macrocyclic ethers (crown ethers)[107] are able to be coordinated to alkali metal cations and to separate the complex ion pair formed by the base[108,109], investigators of the elimination mechanism acquired a valuable instrument for the elucidation of the role of ion pairs in *syn*- or *anti*-elimination. Such information can be obtained by comparing the steric results of the reaction of a given compound with a base in the presence and absence of the crown ether.

Data have been published[110] for the reaction involving elimination from *trans*-2-phenylcyclopentyl toluene-p-sulphonate in the t-BuOK–t-BuOH system at 50°C. In the absence of the crown ether, the ratio of 1-phenylcyclopentene (the *syn*-elimination product) and 3-phenylcyclopentene (the *anti*-elimination product) was 9.8–11.8 (depending on the reaction time). After the addition of the macrocyclic ether (dicyclohexyl-18-crown-6) in an amount equal to that of the base, the ratio became 0.43, i.e. the steric course of the reaction was altered sharply. An analogous result was achieved[111] also in the reactions of other alicyclic toluene-p-sulphonates with t-BuOK. The addition of the crown ether in this instance also drove the reaction along the *anti*-elimination pathway.

An interesting result was likewise obtained[112] in a study of the linear 5-decyl toluene-p-sulphonate with t-BuOK in t-butyl alcohol, benzene, and dimethylformamide (DMF). It was found that the base in the form of an ion pair and the ions separated by the crown ether are involved only in *anti*-elimination but in quite different ways: in the former case the product is mainly a *cis*-olefin and in the latter a *trans*-olefin. The influence of the crown ether is then manifested only in t-butyl alcohol and in benzene, while in DMF the ratio of the reaction products does not change when the crown ether is added. This finding evidently shows that in DMF the base exists in a fully dissociated state also in the absence of the crown ether. Thus the use of crown ethers established that weakly polar and protic solvents promote the reaction via the *syn*-elimination pathway, while in polar aprotic solvents *anti*-elimination predominates. Furthermore, it follows from these experiments that in the bimolecular reaction *syn*-elimination is caused by the base in the form of a close ion pair, while *anti*-elimination proceeds under the influence of the separated ions. The use of crown ethers for the investigation of the $E1cB$ mechanism is described by Hunter et al.[113]

Numerous studies in recent years were devoted to the stereochemistry of $E2$ reactions in alicyclic systems. The discovery that the *syn*-elimination accelerated by bases in the series of *trans*-2-arylcyclopentyl toluene-p-sulphonates (VII) is faster than the *anti*-elimination for the *cis*-isomers (VIII) leads not only to the conclusion that *syn*-elimination is a concerted reaction[93] but also indicates the dependence of the relative rates of synchronous elimination on the dihedral angle[100].



$$k_{syn}/k_{anti} = 9.1\ (Z = H);\quad \rho_{syn} = 2.8;\ \rho_{anti} = 1.5;\quad k^H/k^D = 5.6\ (50^\circ C)\ . \qquad (3)$$

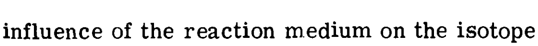
The large *syn/anti* ratio, the more positive value of ρ for the *syn*-process, and an isotope effect which is close to a maximum, together with the undoubted second-order kinetics constitute rigorous proof of a *syn*-coplanar $E2$ mechanism with an appreciable carbanionic character (*H* transition state, see Figure). Owing to conformational limitations, *anti*-elimination from the *cis*-toluene-*p*-sulphonates (VIII) proceeds via an "$E1$-like" mechanism.

Preferential *syn*-elimination has also been demonstrated in a series of cyclo-octyl[25] and cyclodecyl[94,114–116] derivatives. Mainly *exo*-*cis*-bimolecular elimination predominates in the series of norbornyl derivatives[117–123]. In addition, it has been shown that the rate of reaction is strongly influenced by the steric strain in the ring. Thus the relative rates of β-elimination in the series of cyclopentyl, cyclohexyl, cycloheptyl, and cyclo-octyl toluene-*p*-sulphonates are 16.25, 1.0, 12.62, and 152.0 respectively[124].

The report of the synthesis of bridged olefins[125–129] initiated a new stage in the chemistry of bridged compounds. These olefins were obtained by the Hofmann cleavage of quaternary ammonium compounds and dehydrochlorination in the presence of collidine[129]. Bicyclo-[3,3,1]non-1-ene is also synthesised from a salt of *endo*-2-methanesulphonoxybicyclo[3,3,1]nonane-2-carboxylic acid[126]. The synthesis of these compounds constitute an evident infringement of Bredt's rule.

3. Isotope Effects in $E2$ Elimination

The primary isotope effects in the $E2$ mechanism should be observed when a labelled base, labelled α-carbon and β-carbon atoms, labelled group X to be eliminated, and labelled α-hydrogen are used. Secondary isotope effects can occur for α-hydrogen atoms and the non-eliminated β-hydrogen atoms. The isotope effect may then serve as a criterion for the elucidation of the structure of the transition state[130,131]. The isotope effect of the solvent (the replacement of water by D_2O) is studied for this purpose[132]. Saunders and Edison[133] found that the isotope effects k^H/k^D for compounds (IX, $Z = R^1 = R^2 = H$) with different leaving groups (X = Br, OTs, $\overset{+}{S}Me_2$, and $\overset{+}{N}Me_3$) are respectively 7.11, 5.66, 5.07, and 2.08. This series agrees with the increase of the carbanionic character of the activated complex and may be identified with the gradual transition from the *B* region to the *H* region (see Figure). Such changes should be accompanied by an increased shift of the β-hydrogen from the carbon atom to Y and thus by a decrease of the isotope effect, which is in fact observed. A similar result was obtained in another study[126].



$$\bar{Y} + Z{-}C_6H_4{-}\underset{}{CH(R^1)}{-}CH(R^2){-}X \rightarrow YH + Z{-}C_6H_4{-}C(R^1){=}CH(R^2) + \bar{X} \quad . \qquad (4)$$

(IX)

The influence of the reaction medium on the isotope effect has been observed in reactions of dimethyl-(β-phenylethyl)sulphonium salts (IX, $Z = R^1 = R^2 = H$, $X = \overset{+}{S}Me_2$).[134,135] The rate of the reaction of the HO^- ion with sulphonium bromide in a water–DMSO mixture increases sharply with increased DMSO content and the isotope effect of the medium k^{32}/k^{34} diminishes from 1.0074 in pure water to 1.0011 in ~20% DMSO. The β-hydrogen isotope effect in this range of solvent compositions does not vary appreciably, but, when the DMSO content increases still further, the ratio k^H/k^D passes through a maximum and then decreases again. The influence of the added DMSO was interpreted by the authors as a result of the increase of the effective base strength owing to a change in the degree of solvation, which displaces the activated complex in the direction of the carbanion-like transition state (from the *B* region to the *H* or *G* region). This should lead to a decrease of the polarisation of the α-C–S bond in the transition state, which entails a decrease of the sulphur isotope effect. On further increase of the DMSO content, the stability of the carbanion increases and the activated complex now becomes more reactant-like (i.e. shifts from the *C* region in the direction of the *A* region) in conformity with Hammond's postulate[62]. If it is supposed that in 20% DMSO the β-hydrogen in the transition state is transferred to the base Y to an extent greater than 50%, the addition of DMSO should initially lead to a transition state with a symmetrically linked β-hydrogen atom (to which corresponds the maximum value of k^H/k^D) and then to a state in which the β-hydrogen atom is displaced towards Y to an extent less than 50% (decrease of k^H/k^D) and this was in fact observed in the study quoted above[135]. Thus, when the DMSO content is increased, the position of the saddle point on the potential energy surface illustrated in the Figure will be displaced from the *B* region in the direction between the *G* and *H* regions and then back again towards the *A* region.

Willi[85] determined the primary isotope effects for the reactions of 2-deutero-2,2-diphenylethyl-*p*-Z-benzenesulphonates with sodium methoxide in methylcellosolve for Z = OMe, H, and NO_2 and obtained 5.27, 5.42, and 6.70 respectively. It appears that, when Z = OMe, the activated complex is in the *H* region and has a more pronounced carbanionic character. On passing to *Z* = H and NO_2, the degree of transfer of the β-hydrogen to the base diminishes, which brings it closer to the symmetrical position. β-Hydrogen isotope effects in $E2$ reactions have also been investigated in other studies[64,136–143].

In recent years data concerning the presence or absence of the β-hydrogen isotope effect have been widely used to solve the problem whether the $E2$ reaction proceeds via the *syn*- or *anti*-elimination mechanism in various systems[94,97,114,144–150]. It was shown[119,151,152] that *syn*-elimination predominates in norbornyl and bicyclo[2,2,2]-octyl derivatives. In these compounds $(k^H/k^D)_{anti} > (k^H/k^D)_{syn}$.

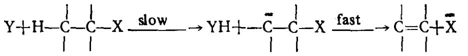
Finley and Saunders[153] carried out an extensive study of the primary β- and secondary α- and β-hydrogen isotope effects in the $E2$ reactions of cyclohexyl toluene-*p*-sulphonates in the presence of EtONa–EtOH and t-BuOK–t-BuOH. Both secondary isotope effects (α- and β-) are large (k^H/k^D = 1.14–1.15 and 1.36–1.51), while the primary β-effect is higher in t-butyl alcohol (k^H/k^D = 7.53) than in ethanol (k^H/k^D = 4.47). The structure of the activated complex in this reaction apparently corresponds to the "central" complex (*B* region, see Figure). The large secondary isotope effects are due to the appreciable sp^2 character of the α- and β-carbon atoms in the transition state. If this is so, then the primary β-hydrogen isotope effect in ethanol will correspond to the transition state in which the hydrogen atom is transferred from the β-carbon atom to the base Y to an extent less than 50%. The activated complex in t-butyl alcohol should then move in the direction of the symmetrical state acquiring at the same time carbanionic character and leading to an increase of the isotope effect, which has in fact been observed[153].

IV. THE *E*1*cB* MECHANISM

1. General Characteristics of β-Elimination Via the *E*1*cB* Mechanism

The *E*1*cB* mechanism is the third β-elimination mechanism proposed by Ingold[154]. It differs from the usual *E*2 mechanism by the fact that it corresponds to a two-stage process involving the formation of an intermediate discrete carbanion, while *E*2 elimination is a synchronous process proceeding via a single transition state from the substrate to the product[2,154]. Two main types of this mechanism are distinguished:

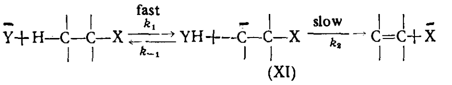
(1) Type *A*, in which the first rate-limiting stage is the bimolecular formation of a carbanion and the second stage is the relatively rapid removal of the leaving group from the α-carbon atom:



$$Y + H{-}\overset{|}{\underset{|}{C}}{-}\overset{|}{\underset{|}{C}}{-}X \xrightarrow{\text{slow}} YH + {-}\overset{-}{\underset{|}{C}}{-}\overset{|}{\underset{|}{C}}{-}X \xrightarrow{\text{fast}} \overset{|}{\underset{|}{C}}{=}\overset{|}{\underset{|}{C}} + \bar{X} \quad . \qquad (5)$$

(X)

(2) Type *B*, in which the first stage is the rapid reversible formation of a carbanion, while the second, rate-limiting stage involves the unimolecular decomposition of the carbanion; if the base is not in this case the lyate ion derived from the solvent, whose conjugate acid YH may be present in excess, second-order kinetics are observed:



$$\bar{Y} + H{-}\overset{|}{\underset{|}{C}}{-}\overset{|}{\underset{|}{C}}{-}X \underset{k_{-1}}{\overset{\text{fast}\ k_1}{\rightleftharpoons}} YH + {-}\overset{-}{\underset{|}{C}}{-}\overset{|}{\underset{|}{C}}{-}X \xrightarrow[k_2]{\text{slow}} \overset{|}{\underset{|}{C}}{=}\overset{|}{\underset{|}{C}} + \bar{X} \quad . \qquad (6)$$

(XI)

Second-order kinetics are usually observed for both types of the *E*1*cB* mechanism, as for the bimolecular *E*2 mechanism, since there is no kinetic criterion for distinguishing these mechanisms. If the pre-equilibrium carbanionic elimination (type *B*) takes place in protic solvents, then the β-hydrogen atoms of the substrate can exchange for the solvent protons at a rate exceeding the rate of elimination. Such exchange may be observed either by using a labelled substrate in an unlabelled solvent or conversely by using an unlabelled substrate in a labelled solvent. The occurrence of deuterium exchange is evidence for a pre-equilibrium *E*1*cB* mechanism; on the other hand, the absence of exchange indicates an irreversible *E*1*cB* mechanism (type *A*) or an *E*2 mechanism.

Breslow[155] suggested that, depending on the relative energetics, rapid hydrogen exchange may be an unrelated side reaction in *E*2 elimination. However, this hypothesis has been criticised[6,156,157]. In particular, Hine et al.[156], who investigated the elimination of HF from 2,2-dihalogeno-1,1,1-trifluoroethanes, established that in a methanol solution of methoxide the compounds exchange hydrogen at a significantly higher rate than that of their elimination reaction. The activating influence of the α-fluorine atoms and β-halogen atoms together with the well known difficulty of eliminating fluorine in the form of an anion from a saturated carbon atom (even more so from a carbon atom linked to other halogen atoms[158,159]) make it very likely that a carbanion is formed in this elimination reaction. Hine et al.[160] believe that, if the carbanion is formed, then in all probability it is an intermediate in the elimination reaction, since the transfer of its free electron pair should accelerate the formation of the olefin more effectively than the partial transfer of the same electron pair in the *E*2 transition states. In his study of the k_{OTs}/k_{Br} ratio as a criterion of the degree of dissociation of the C–X bond Hoffmann[161] also concluded that all the experimental examples known hitherto confirm this hypothesis. Thus the conditions and structures which ensure the formation and stabilisation of the carbanion favour the *E*1*cB* mechanism. The formation of a carbanion requires the abstraction of a proton from the CH acid. In elimination reactions bases are always used for this purpose. However, the presence of activating substituents, similar to the nitro- and carbonyl-groups, as well as other substituents with strong *–I* and *–M* effects may increase the acidity of the β-hydrogen to such an extent that the compound may give rise to a carbanion without the addition of an external base—the alkalinity of glass, for example, may be sufficient for this purpose. All the factors responsible for both the formation and stabilisation of carbanions are widely discussed in Cram's book[162]. These problems have been considered in a number of reviews[11,12,163-167] in relation to the elimination reaction. The influence of solvents on the reactions of carbanions is discussed in Ritchie's review[168].

Crosby and Sterling[169-171] investigated the influence of 17 activating groups on the rate and mechanism of the reaction

$$\bar{Y} + Z{-}CH_2CH_2{-}X \rightarrow Z{-}CH{=}CH_2 + \bar{X} + YH \quad , \qquad (7)$$

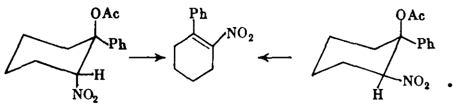
where X is the leaving phenoxy-group and Z represents activating substituents, which are listed below in order of decreasing activating influence:

$$NO_2,\ \overset{+}{P}Ph_3,\ \overset{+}{S}Me_2,\ COMe,\ CHO,\ SO_2OEt,\ SO_2Ph,\ SO_2Me,$$
$$CN,\ COOEt,\ SO_2N(CH_2Ph)_2,\ SOPh,\ CONH_2,\ SOMe,$$
$$CONEt_2,\ \overset{+}{N}Me_3,\ COO^-.$$

On passing from NO_2 to SOMe in this series, the reaction rate constant diminishes by a factor of 10^6. The rate constants are correlated with σ_R^-, but not with σ and σ*. This shows that the resonance stabilisation of the carbanion is an important factor in the activation of such systems. Furthermore, a satisfactory correlation is observed between the reaction rate constant and pK_a and the ionisation rate constant of the $Z-CH_3$ acid (a CH acid) as well as the rate constants for the nucleophilic addition of alkoxides to a series of vinyl compounds of the type $Z-CH=CH_2$.[172] Bearing in mind together with these findings the low values of the isotope effect and the reaction constant ρ as well as its insensitivity to changes in the substituents attached to the leaving phenoxy-group, the authors[169-171] concluded that elimination from these phenoxyethyl compounds proceeds via a pre-equilibrium *E*1*cB* mechanism at least for sulphoxides (Z = SOMe) and for compounds more reactive than the latter.

Rappoport and coworkers[173] compared the results obtained by Crosby and Stirling with data for the addition of various nucleophiles[172,174-180] and for nucleophilic vinyl substitution (which proceeds via addition and elimination)[181] with the approximate ionisation rate constants k_i and the dissociation constants K_a of the CH acids $Z-CH_3$[182] (for all the Z investigated by Crosby and Stirling). He concluded that all the data rigorously confirm the hypothesis of the *E*1*cB* mechanism of reaction (7).

The methoxide-catalysed *anti*- and *syn*-elimination of HOAc from the nitroacetates (XII) and (XIII) and the elimination of HOMe from the corresponding methoxy-compounds have been compared[183].



(XII) (XIII) (8)

It was established that the elimination of HOMe involves the reversible formation of a carbanion on treatment with MeOH–MeONa (*E*1c*B* mechanism, type *B*). Having considered the relative reaction rates, the effect of substituents, the deuterium isotope effects, and the activation parameters for the reactions of the acetoxy- and methoxy-compounds, the authors[183] concluded that elimination from both (XII) and (XIII) proceeds via an intermediate carbanion and that elimination with participation of mobile protons activated by the NO_2, MeCO, and CN substituents in general usually proceeds via the carbanionic mechanism.

This conclusion[183] is in full agreement with the conclusions reached by Crosby and Stirling, because the above substituents include the series of activating groups for which the *E*1c*B* mechanism has been demonstrated. It has been established[184] that the reactions of these compounds as well as their 4,4-dimethyl analogues in the presence of pyridine in $CHCl_3$–EtOH also proceed via the *E*1c*B* mechanism. For this reaction, the activation energy $E_a = 6.9$ kcal mole^{-1}, the activation entropy $\Delta S^{\neq} = -50$ e.u., the isotope effect $k^H/k^D = 4.5$, and the reaction constant $\rho = 1.45$, which is in full agreement with the proposed mechanism. A study[185] of the elimination of methyl alcohol from the isomeric *cis*- and *trans*-1-methoxy-2-nitro-1-phenylcyclopentanes also demonstrated the operation of a carbanionic mechanism for both isomers. Carbanionic mechanisms have been shown to occur in the elimination of substituted benzoic acids from 4-aroyloxy-2-butanones with formation of vinyl ketones[186], in the elimination of water from 2-cyano-1-hydroxy-2-(*p*-nitrophenyl)ethane[187], and in the elimination of AcOH from 9-acetoxy-10-methyl-*cis*-2-decalone[188]. Evidently, in all the examples β-hydrogen is activated by one of the groups which Crosby and Stirling investigated. Particular mention should be made of studies[189-191] which established convincingly by detailed kinetic investigations and the investigation of isotope effects that the β-elimination of water from 9-fluorenylmethanol in aqueous alkaline media and in alcohol proceeds via an *E*1c*B* mechanism with a slight contribution by the *E*2 mechanism.

The scope of this review does not allow a detailed consideration of the studies devoted to β-elimination from carbamates, various sulphones, etc.[192-196], for which the *E*1c*B* mechanism has been demonstrated.

There can now be no doubt about the possibility of β-elimination in activated systems by a carbanionic mechanism. Extensive studies have been carried out in this field on the influence of activating groups on the mobility of β-hydrogen and on the stabilisation of the carbanion formed. Furthermore, intensive research into the influence of the medium and bases on the kinetics and mechanism of this reaction is being prosecuted.

2. Stereochemistry of β-Elimination via the *E*1c*B* Mechanism

The hypothesis of complete *trans*(*anti*)-stereospecificity of *E*2 reactions was adopted at an earlier stage. It was confirmed for almost all the examples investigated and the manifestation of *trans*-specificity in the reaction was therefore regarded as sufficient evidence to assume the *E*2 mechanism. Any breakdown of this stereospecificity was therefore regarded as evidence for the operation of another mechanism. In particular *syn*-stereospecificity was frequently accounted for by the *E*1c*B* mechanism. However, now that it is known that an *E*2 reaction can be both *anti*- and *syn*-stereospecific, the occurrence of *syn*-elimination should not apparently be regarded as evidence for elimination via the *E*1c*B* mechanism. Nevertheless, Ingold[197] emphasised that the *E*1c*B* mechanism should be either *syn*-stereospecific or non-stereospecific. We shall now consider to what extent this postulate actually holds in relation to the available experimental facts.

Jones et al.[198] synthesised diastereoisomeric 5-butyl-2-hydroxycyclohexyl-*p*-tolyl sulphones and measured the rates of piperidine-catalysed bimolecular elimination DMSO for the corresponding *trans*,*trans*-, *cis*,*trans*-, and *trans*,*cis*-isomeric sulphonate esters. Since a conjugated sulphone is the only product of these reactions, the implication is that two of these sulphonates undergo *syn*-elimination, while the *cis*,*trans*-isomer undergoes *anti*-elimination (formally diequatorial elimination). The relative rates change at most by a factor of 1.4 and are insensitive to the nature of the leaving group (either OTs or OMe). The *trans*,*cis*-compound (axial OSO_2R), axial SO_2Ar) reacted faster. The addition of piperidine hydrochloride causes a slight but nevertheless appreciable decrease of the rate. However, when the reaction is carried out in a deuterated solvent, the takeup of deuterium is insignificant. These data were explained by a mechanism with irreversible formation of a carbanion (*E*1c*B*, type *A*). Preliminary investigation of analogous isomeric 4-t-butyl-2-chlorocyclohexyl phenyl sulphones yielded additional facts confirming the above conclusions (see also Refs. 199 and 200).

The base-catalysed elimination of acetic acid from 2-nitro-1-phenylcyclohexyl acetates (XII) and (XIII) proceeds via a carbanionic mechanism, since the *syn*-elimination from (XII) is faster than the *anti*-elimination from (XIII). An appreciable deuterium isotope effect was observed; both processes show similar sensitivities to changes in temperature, medium, and substituents[184, 201]. The inclusion of *gem*-dimethyl groups in the 4-position increases the rate of elimination from (XII) and decreases the rate of elimination from (XIII). Furthermore, the corresponding nitronate ion was detected spectrophotometrically during the reaction in a study[184,185] of methoxy-analogues of (XII) and (XIII). Comparison of kinetic data, isotope effects, and the influence of substituents for the acetoxy- and methoxy-derivatives established the occurrence in these reactions of carbanionic processes of three types[183]: with an irreversible second-order carbanionic mechanism for (XII) and (XIII), with a reversible second-order carbanionic mechanism for the methoxycyclohexyl compounds, and with an irreversible first-order carbanionic mechanism (see below) for the methoxycyclopentyl compounds $\{k_1$ is the rate constant for the rate-limiting stage and $k_2 \gg k_{-1}[BH]\}$. The study of Bordwell et al.[183] yielded convincing evidence for a carbanionic mechanism of the *syn*- and *anti*-elimination from these compounds. Ring deformation apparently plays an important role in these processes. Special mention was made of the fact that the synchronous *anti*-*E*2 mechanisms for compound (XII) and its methoxy-analogues did not compete with the carbanionic process. Thus both *syn*- and *anti*-elimination proceed in this instance via an intermediate carbanion.

In the base-catalysed dehydrochlorination of the diastereoisomeric 1-chloro-1,2-diphenyl-2-toluene-*p*-sulphonylethanes[202], the *erythro*- and *threo*-isomers underwent full *trans*- and *cis*-elimination respectively. Thus both diastereoeisomers yielded 2-toluene-*p*-sulphonyl-*cis*-stilbene. The authors suggest a synchronous mechanism for the *erythro*-isomer and a carbanionic mechanism for the *threo*-isomer. The same system was studied in another investigation[203].

The amine-accelerated elimination of HF from fluoroethanes activated by the sulphonyl group is *syn*-stereospecific[204]. The study of the isotope effect in this reaction indicates an *E*1*cB* mechanism involving the formation of an ion pair (see also Hunter and Shearing[205]).

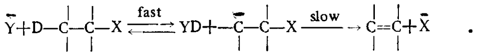
There have been very few studies on the stereochemistry of the *E*1*cB* mechanism. However, the available examples have shown that the mechanism is more likely to be *syn*-stereospecific than *anti*-stereospecific: this is in its turn consistent with Ingold's hypothesis[197].

3. Isotope Effects in the *E*1*cB* Elimination

We considered above two generally accepted types of the *E*1*cB* mechanism. If the formation of the carbanion is the rate-limiting stage (type *A*), then the primary kinetic isotope effects should occur for the labelled base Y the β-carbon atom, and the eliminated β-hydrogen atom. Whether or not secondary isotope effects are observed under these conditions for the α-hydrogen atoms or the non-eliminated β-hydrogen atoms should probably depend on the change in the hybridisation of the β-carbon orbitals on formation of the carbanion. Since the carbanion decomposes solely into the reaction products, the observed rate should not be sensitive to isotope substitution at the α-carbon atom or in the leaving group X. On the other hand, if the formation of the carbanion (XI) is a fast and reversible stage and its conversion into the reaction products is rate-limiting (type *B*), primary kinetic isotope effects should be observed for the labelled group X, α-carbon, and β-carbon, while in the case of a labelled group Y and labelled β-hydrogen atoms, equilibrium isotope effects may be observed. Secondary isotope effects may occur also for α'-hydrogen atoms.

There are few literature data for isotope effects in *E*1*cB* reactions involving labelled Y, α-carbon, or X. Almost all the isotopic studies have been carried out with labelled β-hydrogen. The β-hydrogen isotope effects are characteristic of both *E*2 reactions and *E*1*cB* (type *A*) reactions. The latter can therefore be distinguished only by comparing the magnitudes of these effects[130,131].

The situation is much more complex for the *E*1*cB* (type *B*) mechanism. *E*2 and *E*1*cB* (type *A*) reactions can proceed with a normal isotope effect, characterising these mechanisms, while the *E*1*cB* (type *B*) mechanism will exhibit only a small equilibrium isotope effect reflecting the different equilibrium concentrations of carbanions in reactions (6) and (9):[35]



$$\bar{Y}+D-\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}-X \xrightleftharpoons{\text{fast}} YD+-\overset{-}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}-X \xrightarrow{\text{slow}} \overset{|}{\underset{|}{C}}=\overset{|}{\underset{|}{C}}+\bar{X} \quad . \qquad (9)$$

In this case definite conclusions can be reached only by comparing the rates of elimination of the unlabelled substrate in the unlabelled solvent with the rate of elimination of the labelled substrate in the labelled solvent. A normal isotope effect will be observed if the reaction proceeds via the *E*2 or *E*1*cB* (type *A*) mechanism, while the equilibrium isotope effect (the isotope effect of the solvent) will obtain for the *E*1*cB* (type *B*) mechanism. If, as frequently happens, YH and YD are solvents, the effective concentrations are constant and equal and the ratio of the observed rates is then equal to the ratio of the isotopic equilibrium constants[35]. Depending on the bond energy in RH relative to YH, the above ratio can vary from a value less than unity (the usual case) to one slightly greater than unity.

In the elimination of methanol from 4-methoxy-2-butanone and 4-methoxy-2-pentanone with formation of 3-but-2-enone and 3-pent-2-enone via the *E*1*cB* mechanism the exchange of β-hydrogen atoms (in the α-position relative to the carbonyl group) with D_2O-OD^- is rapid and the overall isotope effect $k^H_{obs}/k^D_{obs} = 0.87$ and 0.77 respectively[206]. In full conformity with the *E*1*cB* (type *B*) mechanism, Crosby and Stirling[171] also observed a rapid exchange in the elimination of phenol from dimethyl-(2-phenoxyethyl)sulphonium iodide and methyl-2-phenoxyethyl sulphone ($k^H_{obs}/k^D_{obs} = 0.66$ and 0.78 respectively).

When acetic acid was eliminated from 2-acetoxy-1-nitro-2-phenylcyclohexanes and the corresponding cyclopentanes and in the elimination of methanol from *trans*-2-methoxy-1-nitro-phenylcyclopentane[183,184], large β-hydrogen isotope effects ($k^H_{obs}/k^D_{obs} = 4.9-8.1$) were observed in all the reactions, as expected for the *E*1*cB* (type *A*) mechanism with a more or less symmetrical transfer of β-hydrogen from β-carbon to Y.

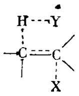
Yet another version of the *E*1*cB* mechanism was investigated by Rappoport[207-213] and Bordwell et al.[185] (see also Refs. 190, 195, 197, 198). If the entire substrate is converted into a carbanion under the influence of the base in the rapid stage of the reaction, further addition of the base no longer has any effect on the concentration of the carbanion and the elimination proceeds subsequently as a pseudo-first-order reaction. There is no isotope effect in such reactions, since the molecule no longer contains the isotopic atom in the rate-limiting stage. When HCN was eliminated from 2,6-dimethyl-4-(1,1,2,2-tetracyanoethyl)aniline in the presence of triethyl- or tri-n-butylamine, $k^H/k^D = 0.93$ was found[214]. Bordwell et al.[185] obtained $k^H/k^D = 1.7$ for the elimination of methanol from *trans*-2-methoxy-1-nitro-2-phenylcyclopentane using NaOMe–MeOH; k^H/k^D for the first stage (the formation of a carbanion) was normal and equal to 7.5. The same value was obtained for the formation of a carbanion from 2-nitro-1-phenylpropane using sodium t-butoxide in t-butyl alcohol[183].

When water is eliminated from 9-fluoroenylmethanol, different β-hydrogen isotope effects are observed in water and methanol, the exchange being faster than elimination in both water and methanol[191,215]. In agreement with the results of the majority of the above studies, the isotope effects in the exchange processes are large ($k^H/k^D \simeq 7$). For water, the overall isotope effect (the isotope effect of the solvent) is $k^H/k^D = 0.92$ (the rate of reaction of the unlabelled substrate in unlabelled water was compared with the rate of reaction of the labelled substrate in labelled water[215]). The corresponding value for methanol is 0.36. Such an isotope effect of the solvent should in fact be expected for the reversible substrate–carbanion stage when the *E*1*cB* (type *B*) mechanism operates. It is unlikely that a combination of the primary isotope effect and the isotope effect of the solvent would give rise to such a low overall value of k^H/k^D for the *E*2 mechanism. However, More O'Ferrall and Slae[215] concluded on the basis of a detailed analysis of the initial rates of reaction of a labelled substrate in a labelled solvent and of an unlabelled substrate in an unlabelled solvent that the competing *E*2 mechanism nevertheless makes a slight contribution to the reaction.

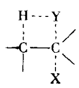
Thus it is seen from the data described above that the study of the isotope effects using substrates labelled in various positions makes it possible to distinguish both different mechanisms and different types of the same mechanism. The *E*2 and *E*1*cB* (type *A*) mechanisms can be distinguished by studying the isotope effects for substrates with labelled α-carbon or X.

V. THE *E*2*H*–*E*2*C* MECHANISMS

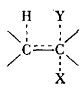
As early as 1956, de la Mare and Vernon[216] demonstrated the greater effectiveness of a weak base (the thiophenoxide ion) compared with a strong base (the ethoxide ion) in the elimination reaction which they catalysed (see the review of Saunders and Cockerill[163]). After this, it was frequently shown that very easy elimination is induced also by other weak bases, particularly halide ions in dipolar aprotic solvents[3,6,217–222]. Some workers[3,6,221–222] claimed that these reactions are more or less normal *E*2 reactions, but Winstein and coworkers[223] suggested that they be put in a separate *E*2*H*–*E*2*C* group, which was also supported by other workers[224,225]. It is suggested that, in the *E*2*H*–*E*2*C* range of mechanisms, the removal of β-hydrogen in the elimination reaction is accompanied to a greater or lesser extent and activated by attack by the Y base on the α-carbon atom ("from the rear" in relation to the C–X bond), as shown in models of activated complexes:



(XIV)
*E*2*H*



(XV)



(XVI)
*E*2*C*

It is seen from the models that (XIV) does not differ in any way from the central synchronous *E*2 mechanism; (XV) and (XVI) differ primarily by the fact that the base Y attacks α-carbon and not β-hydrogen as in the *E*2 mechanism. This in fact makes them similar to the transition state in the S_N2 substitution reaction, and for this reason all *E*2*H*–*E*2*C* mechanisms are combined under the general name "concurrent mechanisms". A characteristic feature of these reactions is that they are more effectively accelerated by weak bases provided that the latter are strong nucleophiles; the ratio of the products and certain characteristics of the reaction are altered somewhat under these conditions.

For example, treatment of secondary butyl and pentyl bromides as well as the corresponding toluene-*p*-sulphonates with strong nucleophiles and very weak bases in dipolar solvents (NBu_4Br in DMSO containing 2,6-lutidine) yields mainly the *trans*-olefin, in agreement with Zaitsev, while the reaction with a strong base and a weak nucleophile (t-BuOK–t-BuOH) yields mainly the *cis*-olefin, in agreement with Hoffmann[224]. Another communication[225] reported the influence of the alkyl, aryl, benzyl, bromo-, and methoxycarbonyl substituents on the rate of bimolecular elimination; according to the authors, the spectra of transition states ranging from *E*2*H* to *E*2*C* are obtained and the sensitivities of various transition states to changes in substituents are very different. The *E*2*C* transition state, which is olefin-like, gives a high yield of the most stable isomer (the *trans*-olefin according to Zaitsev), provided that the requirement that the hydrogen atom and the leaving group are in the *anti*-positions is not too rigorous. Similar results are quoted in other papers by Parker and coworkers[223,226–229].

McLennan and Wong[230] determined $\rho = 2.11$ for the dehydrochlorination of $(p\text{-}RC_6H_4)_2CHCCl_3$ (R = OMe, Me, H, F, Cl, Br, or NO_2) in ethanol at 65°C, which is accelerated by sodium thiophenoxide. For the S_N2 reaction involving the substitution of chlorine by thiophenoxide in $(p\text{-}RC_6H_4)_2CHCHCl_2$ (R = OMe, Me, H, Cl, Br), which leads to $(p\text{-}RC_6H_4)_2C{=}CHSPh$, $\rho = 0.41$. Comparison of these values with that obtained for an *E*2 reaction in the presence of $Et\bar{O}{-}EtOH$ ($\rho = 2.34$) led the author to the conclusion that in the latter case dehydrochlorination proceeds via an *E*2*H* transition state. The transition state in dehydrochlorination by a thiolate ion is *E*2*C*-like according to the author.

However, there have been very few studies on this problem; conclusions are frequently reached on the basis of secondary factors and those arrived at by one investigator are frequently disproved by others. Thus Parker, Winstein, and coworkers[223,224,231] proposed an *E*2*C* mechanism for the reactions of secondary and tertiary butyl halides in acetone under the influence of weak bases (halide ions), while the results of Eck and Bunnett[232] conflict with this finding. It has been shown that, in the β-elimination of HBr from 2-bromo-2,3,3-trimethylbutane and from t-butyl bromide in acetone or dioxan, induced by chloride ions, the more "hindered" substrate reacts faster than the less "hindered" one[232]. This finding shows that the ion of the base does not approach the α-carbon atom in the transition state as required by the *E*2*C* mechanism. Bunnett pointed out in his argument against the validity of the *E*2*C* mechanism (and the necessity for it)[6,223] that elimination in such systems proceeds via the normal *E*2 mechanism (*E*2*H* in terms of the new terminology of Winstein and Parker), but the relative nucleophilic reactivity of RS^-, RO^-, and tentatively Cl^- in relation to β-H depends on the degree of binding of the given base to the hydrogen in the transition state. When the base is strongly bound to the hydrogen, the alkoxide ion is more reactive, but, when the base interacts with β-hydrogen only slightly, the thiolate ion is a more effective base for the acceleration of an *E*2 reaction.

At any rate, as long as our understanding of the way in which the change in the solvating capacity of the solvent influences carbonium ions and carbanions in *E*2 reactions for different substrates with different bases is inadequate, one must be very cautious in adopting a particular view on this problem.

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Examination of the data in this review and the studies which have not been described here owing to lack of space permits certain generalisations concerning the β-elimination mechanism. If the substrate does not contain activating groups at the β-carbon atom but does have a leaving group with an enhanced tendency towards ionisation and an electron-donating substituent at the α-carbon atom, then in a strongly solvating weakly acid medium (in the absence of a base) unimolecular elimination via an *E*1 mechanism takes place for this type of substrate.

On the other hand, if the substrate contains an electron-donating substituent, which increases the electron density at the α-carbon atom, and an electron-accepting substituent, which induces a positive charge on the β-carbon atom, then, when the medium consists of a strong base in an aprotic polar solvent, bimolecular elimination via an $E2$ mechanism takes place. Accordingly, any group which may neutralise the induced positive charge on the β-carbon atom by giving up electrons inhibits the reaction via an $E2$ mechanism.

If the electron-accepting group at the β-carbon atom and the base employed are moderately strong, then elimination proceeds via an "$E1$-like" $E2$ mechanism at a moderate rate. As the electron-accepting capacity of the substituent at the β-carbon atom becomes more pronounced and the strength of the base increases, there is also an increase in the rate of elimination. The elimination mechanism over a certain range of changes of this kind is then gradually altered from the "$E1$-like" type to the central synchronous type and further to the "$E1cB$-like" type, while remaining within the framework of the $E2$ mechanism. On further increase of the electronegativity of the group at the β-carbon atom and of the strength of the base employed, the bond between the β-hydrogen and carbon is weakened to such an extent that the substrate gives up this hydrogen in the form of a proton and forms a carbanion, the $E2$ mechanism being thus converted into an $E1cB$ (type A) mechanism. On the other hand, if the substrate contains a fairly strong electron-accepting group capable of stabilising the conjugate base of the substrate (such as C=O, C=N, NO_2 etc.), then the bond linking the β-hydrogen atom becomes so labile that there is no necessity for a very strong base and even in the presence of weak bases the substrate splits off this hydrogen in the form of a proton during the rapid reversible stage, forming the conjugate base—a carbanion, which loses the leaving group in the subsequent slow stage by a unimolecular process, being converted into an olefin, i.e. an $E1cB$ (type B) mechanism operates.

Thus one may conclude that each of the above specific types of the β-elimination mechanism is, strictly speaking, possible only for a specific compound under fixed conditions and that any changes in the structure of the substrate and in the reaction conditions lead to a shift of the mechanism towards the type which is preferred under the new conditions. Since the transition from one mechanism to another takes place gradually, the simultaneous occurrence of the reaction via two adjacent mechanisms is possible under borderline conditions.

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The Role of One-electron Transfer in Substitution Reactions

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The principal examples of substitution reactions which involve an intermediate one-electron transfer stage are examined. Attention is concentrated on the causes which make this stage important and its relations with other stages in the mechanism are analysed. It is noted that the application of the ideas of one-electron transfer to the mechanisms of all substitution reactions without exception is invalid. Cases of the activation of substitution reactions under conditions favouring electron transfer are discussed. The urgent need for studies in this field is demonstrated and certain tasks for the immediate future are formulated.

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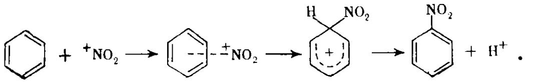
I. INTRODUCTION

The aim of the present review is to discuss the evidence supporting the presence of a one-electron transfer stage in the mechanisms of certain substitution reactions. Numerous studies in which the existence of such a stage explains the observed facts but is justified mainly by logical considerations have been left outside the scope of this review. Attention has been concentrated on reactions for which the existence of an electron transfer stage has been proved. The review includes fundamental examples. The causes which make the electron transfer stage real and the interrelations between this stage and others in the mechanism are discussed. Together with reactions which clearly proceed via a one-electron transfer stage, cases are considered where radical-ions are formed in a secondary reaction pathway and not the main pathway. It is shown that in certain reactions it is possible to increase the yield and rate of formation of the final products by creating conditions favouring the electron transfer stage.

II. THE CONCEPT OF THE ONE-ELECTRON TRANSFER STAGE IN A SUBSTITUTION REACTION

The concept of one-electron transfer as an intermediate stage in inorganic reactions has proved extremely fruitful and is supported by extensive experimental data obtained in the 1940s–1950s. The development of these ideas occurred simultaneously with the development of the foundations of nuclear chemistry and technology[1]. The problem of the role of one-electron transfer in organic reactions was considered during the last 15 years[2-8]. During this period, the development of new methods for the investigation of unstable or relatively unstable species, such as electron transfer products, led to the possibility of their wide-scale investigation. One may say that such species were extremely unfamiliar in organic chemistry during earlier periods.

After the first studies, which drew the attention of organic chemists to the important role of one-electron transfer in reactions, many investigators began to consider the mechanisms of virtually all reactions from the standpoint of oxidation-reduction processes. However, as experimental data accumulated, it was shown that the idea of the one-electron stage should be used in moderation (cf. Okhlobystin[9] and Beletskaya[10]). The hypothesis of one-electron transfer as an intermediate reaction stage presupposes that the reagent and the substrate are involved in an oxidation-reduction interaction. Subsequent stages involve the combination of the products arising as a result of the oxidation-reduction reaction. We shall consider as an example the nitration of benzene[11-13]. The substitution proceeds via the stages in the scheme below[14]:

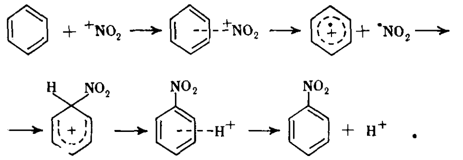


(1)

The process begins with the formation of a π-complex, which corresponds to partial charge transfer. Next the π-complex rearranges to a σ-complex with subsequent elimination of a low molecular weight species—a proton. Within the framework of perturbation theory[14], this is formulated as the formation of a transition state "from the perturbation of the π-system to the perturbation of a definite carbon atom". However, an isolated electron transfer stage is not considered in the perturbation theory[14]. At the same time, it follows from a theoretical study[15] that the approach of the reagent to the substrate bond subjected to attack alters the energy levels of the lowest unoccupied molecular orbital (LUMO) and the highest occupied molecular orbital (HOMO). The intermolecular distance over which the one-electron stage can take place depends on the degree of perturbation. When the distance is large, the products formed in this stage can emerge into the bulk of the reaction solution and when it is small they can recombine in the solvent "cage"[15].

Quantum-chemical calculations[12] have shown that the LUMO of the nitronium cation has an energy of −11.0 eV, while the HOMO of benzene has an energy of −9.24 eV. This makes theoretically probable yet another nitration stage, namely the transfer of an electron (a single charge) from the benzene HOMO to the nitronium cation LUMO;

this stage is represented in the general scheme (2). The species constituting the biradical pair may combine to form a σ-complex:



(2)

Thus one-electron transfer consists in the transfer of a single charge and not of a partial charge as in a π-complex. Partial transfer leads to charge-transfer complexes (CTC), while complete transfer results in the formation of radical-ions, radicals, or ions. The final products may be formed as a result of the combination of radicals derived from the reagent and the substrate, as in scheme (2). Another pathway is also possible, namely the decomposition of the substrate radical-ion with formation of a new radical capable of reacting with a second reagent molecule. This pathway is indicated in relation to the nucleophilic substitution reaction (3).[8] Such reactions are observed among both aromatic and aliphatic compounds and are classified as $S_{RN}1$ reactions:

$$RX \xrightarrow[-Y^{\cdot}]{+Y^-} (RX)^{\overline{\cdot}} \xrightarrow[-X^-]{} R^{\cdot} \xrightarrow{+Y^-} (RY)^{\overline{\cdot}} \xrightarrow[-(RX)^{\overline{\cdot}}]{+RX} RY \quad . \qquad (3)$$

In reactions of the $S_{RN}1$ type the one-electron transfer stage also plays an important role, initiating the transformation and imparting to it a chain mechanism.

We shall consider in greater detail the theoretical postulates and then shall analyse the experimental data characterising the role of one-electron transfer in the mechanism of substitution reactions.

III. THEORETICAL PROBLEMS

1. Thermodynamic Conditions for One-Electron Transfer

Electron transfer can occur only when the difference between the ionisation potential of the donor (I_D) and the electron affinity of the acceptor (E_A) is greater than zero ($I_D - E_A > 0$). In order to determine the sign of this difference, it is possible to compare the HOMO and LUMO energy levels of the substrate and the reagent. For electrophilic and nucleophilic substitution reactions of aromatic compounds, such comparisons can be made using Fig. 1. Evidently the LUMO levels of electrophilic reagents are lower than the HOMO levels of aromatic substrates. In principle, this creates the possibility of electron transfer from the HOMO level of the substrate to the LUMO level of the reagent. For the benzene nitration reaction, this stage was in fact taken into account in scheme (2). Furthermore, Fig. 1 shows that the HOMO level of the hydroxide anion lies above the LUMO levels of substrate molecules, while the HOMO level of the chloride ion lies above the LUMO level of nitrobenzene. Hence it follows that, when an aromatic substrate reacts with a nucleophile, an electron transfer stage is probable.

The calculation whose results are illustrated in Fig. 1 was performed approximately 20 years ago. Naturally, it was necessary to have a later confirmation of these results. Recent calculations by Epiotis[16] showed that relations of the type illustrated in Fig. 1 are confirmed and that they are valid for a wider range of substrates and reagents. Epiotis' study was undertaken to discover the correspondences between the reactivities at individual positions of the substrate molecule and the spin valences of the radical-ion in the same positions. Epiotis based his calculations on the perturbation theory, which, as stated above, does not treat electron transfer as an isolated stage. At the same time the fundamental scheme of orbital interactions obtained by Epiotis for the transition states of electrophilic, nucleophilic, and radical substitutions in aromatic compounds is of great interest for further exposition of the subject (Fig. 2).

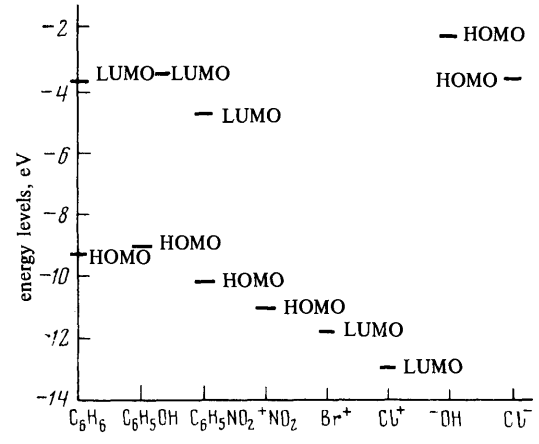


Figure 1. Energy level diagrams for some substrates and reagents in aromatic substitution[12].

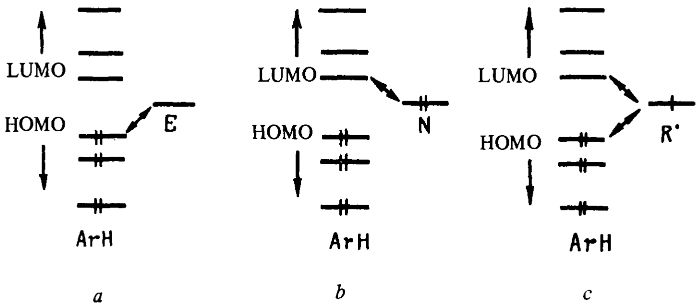


Figure 2. Schematic diagram of the orbital interactions of an aromatic molecule (ArH) with an electrophile (E), a nucleophile (N), and a radical (R·).[16]

Fig. 2 illustrates the types of orbital interactions which are analogous for nucleophilic and electrophilic substitution reactions to those discussed in connection with Fig. 1. For radical substitution, the type of interaction is determined by the nature of the radical R·. If the attacking radical is a nucleophile and has a low ionisation potential, the decisive factor for it is a donor type interaction (with LUMO). For an electrophilic radical with a high ionisation potential the decisive factor should be an acceptor type interaction (with HOMO).

However, one should note that both the calculations of Nagakura and Tanaka[12] and those of Epiotis[16] were performed without taking into account the influence of external substitution factors: solvation and coordination of the species in solution, the formation of hydrogen bonds, steric hindrance, etc. Under certain conditions, these factors may become decisive and may drive the reaction via a different pathway. The nature of the reacting species is also important. Calculations have been made recently[17] in order to determine the tendency of particular reagents to interact with the substrate via ionic or radical-ion pathways. The difference between these pathways is evident from a comparison of schemes (1) and (2). For example, it was found that, when benzene interacts with a proton, the one-electron mechanism is favourable until the substrate and reagents approach one another to a distance of 1.5–2 Å. The reaction of benzene with the nitronium cation can proceed via scheme (2) only over a range of distances from 1.5 to 2.5 Å, while benzene and the extremely reactive methyl cation can interact only via the ionic mechanism whatever the distance.

Electron transfer is preceded by the formation of a charge-transfer complex: $D + A \rightarrow [D^{\delta+}, A^{\delta-}] \rightarrow [D^{+\cdot}, A^{-\cdot}]$. When the CTC is subjected to additional polarisation under the influence of a third molecule (donor, acceptor, or solvent), electron transfer is facilitated[5].

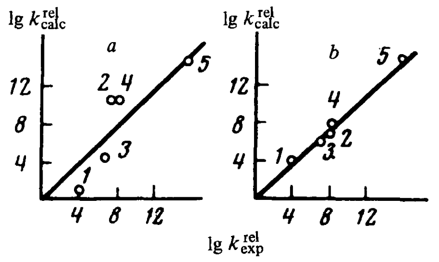


Figure 3. Relation between the experimental and calculated relative rate constants for the exchange of deuterium for protium in heteroaromatic compounds: 1) [3-D]thiophen; 2) [2-D]thiophen; 3) [3-D]furan; 4) [2-D]furan; 5) [2-D]pyrrole[19]; *a*) the values of k^{rel}_{calc} obtained taking into account only the localisation energy, which is proportional to the activation energy for electrophilic substitution; *b*) the values of k^{rel}_{calc} obtained taking into account not only the localisation energy but also the ionisation potential of the molecule involved in the deuterium–protium exchange.

Electron transfer in the reagent–substrate system can occur under the conditions of slight overlapping of the corresponding orbitals or when bridge groups (extraneous ions, solvent molecules) are involved. Electron transfer takes place over an extremely short period, amounting to 10^{-15} s. This is less than the time required for the alteration of the positions of the nuclei of the reacting molecules. Nuclei move over a period of 10^{-13} s or longer[5]. Consequently, the changes in the positions of nuclei take place approximately 100 times more slowly than the change in the electronic state. In conformity with the Franck–Condon principle[5], it is assumed that the positions of the nuclei remain unaltered during electron transfer. This implies that the electron transfer reaction can occur during the extremely short time intervals corresponding to a favourable disposition of the reagent, substrate, and the species present in solution.

2. The Donor–Acceptor Properties of the Reacting Species and the Kinetics of Substitution Reactions

It has been established[18] that the interaction of many heteroaromatic molecules with electrophiles is faster the lower the ionisation potential of the substrate. The calculated rate constants for these reactions agree with experimental values only when models taking into account the electron-donating properties of the heteroaromatic molecule are used[19] (Fig. 3).

The rate constants for the nitration of aromatic hydrocarbons by acetyl nitrate in acetic anhydride, calculated relative to benzene (k^{rel}), vary linearly (Fig. 4) with the ionisation potentials I of the hydrocarbons[20]. There is a similar relation between the ionisation potentials and the relative rate constants for the isotope exchange of hydrogen in an acid medium involving aromatic compounds (Fig. 5).[20]

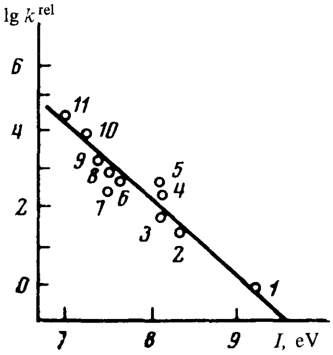
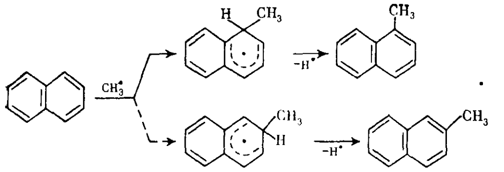


Figure 4. Relation between I and k^{rel} for the nitration of aromatic compounds: 1) benzene; 2) biphenyl; 3) naphthalene; 4) phenanthrene; 5) triphenylene; 6) chrysene; 7) fluorene; 8) fluoranthene; 9) coronene; 10) pyrene; 11) perylene[20].

For radical substitution, the kinetics and direction of the reaction must be determined by the degree of localisation of electron density in individual positions in the molecule and not by its ionisation potential or electron affinity. However, it has been found that the rate of radical substitution in the series of alkylbenzenes varies linearly with ionisation potential, as for other reactions involving states with charge separation[21]. This also confirms the dependence of the site of substitution in the methylation of naphthalene on the polarity of the solvent[22] (acetyl peroxide was used as a source of methyl radicals).

The π-electron density in the naphthalene molecule is distributed non-uniformly: it is greater in the α-position than in the β-position, which ensures the preferential binding of the methyl radical to the α-carbon atom of naphthalene. If the methylation of naphthalene proceeds in accordance with the homolytic substitution mechanism (4), then it is unrelated to the appearance of charged intermediate states. This implies that the site of substitution should not depend on the polarity of the medium.



(4)

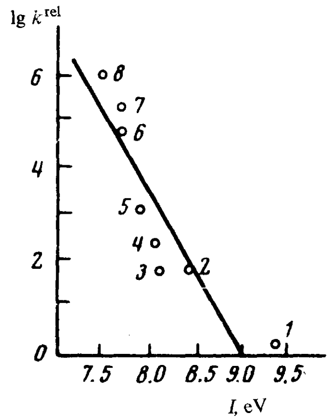


Figure 5. Relation between I and k^{rel} for hydrogen isotope exchange in an acid medium involving aromatic compounds: 1) benzene; 2) biphenyl; 3) terphenyl; 4) naphthalene; 5) chrysene; 6) pyrene; 7) 1,2-benzanthracene; 8) anthracene; 9) perylene[20].

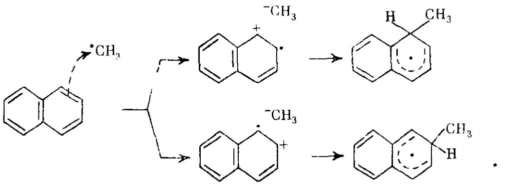
Table 1. The influence of solvent polarity on the selectivity of the homolytic methylation of naphthalene[22].

Solvent	ε*	Ratio of yields of α- and β-methylnaphthalenes	Solvent	ε*	Ratio of yields of α- and β-methylnaphthalenes
Benzene	2.3	7.0	*o*-Dichlorobenzene	9.9	5.8
Chlorobenzene	5.6	6.2	Pyridine	12.3	4.0

*The static dielectric constant ε was adopted as a characteristic of the polarity, which is valid when solvents belonging to a single series of aromatic compounds are compared[23].

In considering reactions (4), one must emphasise that neither the methyl radical nor the naphthalene molecule can themselves be in any way polarised in a polar solvent and give rise to states with separated charges. A dipolar structure is not characteristic of the methyl radical and naphthalene has an ionisation potential too high for this[22]. However, it follows clearly from Table 1 that the selectivity of the homolytic methylation of naphthalene decreases with increasing solvent polarity. The greater the solvent polarity, the more effective the stabilisation of the polar transition state which implies, according to Hammond[24], a greater decrease of the activation energy for the formation of charged species.

In the homolytic methylation of naphthalene the polarity of the solvent has such a significant effect on the reaction selectivity that the authors[22] explained this effect by the formation of species with a unit charge and not merely a fractional charge. Scheme (5) shows how naphthalene radical-cations arise in the interaction between the reagent and the substrate. Here it is important that the degree of stabilisation of the naphthalene radical-cation is independent of whether the positive charge is located at the α- or the β-carbon atom.



(5)

Owing to the stabilisation of the α- and β-"cations" by the polar solvent, the reactivities of the α- and β-position in naphthalene do not differ quite so much and the selectivity of the methylation reaction is accordingly reduced. Whereas in benzene (ε = 2.3) α-methylnaphthalene is formed seven times faster than β-methylnaphthalene, in pyridine (ε = 12.3) the rate of its formation is only four times greater[22].

3. The Site of Substitution and the Distribution of Spin Density in the Radical-Ion of the Reacting Molecule

If the interaction between the substrate and the reagent begins with one electron transfer, a biradical pair should be formed. The nature of the subsequent transformation should depend on the properties of the species involved in the biradical pair. In particular, the substrate radical-ion may be converted into a σ-electron radical with ejection of an ionogenic group. Such interaction of a σ-radical with the reagent leads to a radical-ion of the final product and these species should combine at the site of the radical free valence. If the substrate radical-ion does not show a tendency to eject the ionogenic group, its combination with the radical derived from the reagent is possible. The formation of a new bond is then most probable in the position where the spin density is a maximum. In other words, there should be a correspondence between the nature of the distribution of spin density in the radical-ion and the position which the substituent enters in the corresponding uncharged molecule.

The quantitative characteristics of the distribution of spin density can be obtained from the ESR spectrum of the radical-ion. The ESR spectrum makes it possible to determine the hyperfine interaction constant for the *i*th hydrogen atom a_i^H. This constant is directly proportional to the spin density of the *i*th carbon atom to which the *i*th hydrogen is linked[25].

Under these conditions, different degrees of delocalisation of the unpaired electron in radical-ions with charges of different signs is then possible for the same molecule[26]. Consequently, when electrophilic substitution is considered the site of substitution data must be referred to the properties of the radical-cation, while in nucleophilic substitution correlation with the properties of the radical-anion is required. We may note that the formation of radical-cations or radical-anions has been demonstrated experimentally in the substitution reactions of aromatic compounds[25].

Table 2 shows that the site of electrophilic substitution of aromatic compounds is clearly related to the values of a_i^H for the corresponding radical-cations.

Table 2. Comparison of the properties of a series of aromatic compounds and the corresponding radical-cations.

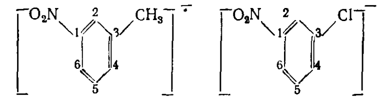
Compound	Reaction	Reactivity in different positions	Order of variation of a_i^H for different positions
NN-Dimethylaniline	Bromination	4 > 2 > 3 (Ref.27)	4 > 2 > 3 (Ref.28)
Naphthalene	Nitration	1 > 2 (Ref.29)	1 > 2 (Ref.30)
Naphthalene	T-H exchange	1 > 2 (Ref.31)	1 > 2 (Ref.30)
Anthracene	Acylation	9 > 1 > 2 (Ref.25)	9 > 1 > 2 (Ref.30
Biphenylene	Nitration	2 > 1 (Ref.32)	2 > 1 (Ref.33)
Azulene	Nitration	1 > others (Ref.34)	1 > others (Ref.35)

When azulene is nitrated, the 1-position is the most reactive[34] and the electron density is a maximum in the same position in the radical-cation[35]. However, in the azulene radical-anion the maximum density is concentrated in the 6-position[36, 37].

Table 3. Comparison of the values of a_i^H and E_{act} for the substitution of chlorine by an ethoxy-group on treatment of chloronitrobenzenes and chlorodinitrobenzenes with an ethanol–piperidine mixture.

Compound	a_i^H in ESR spectrum of radical-anion G, (Refs.38 and 39)	E_{act}, kcal mole^{-1} (Ref.40)
Nitrobenzene	$a_2^H = a_6^H = 3.30$; $a_4^H = 3.82$	—
2-Chloronitrobenzene	$a_6^H = 3.30$; $a_4^H = 3.92$	18.1
4-Chloronitrobenzene	$a_2^H = a_6^H = 3.42$	17.1
1,3-Dinitrobenzene	$a_2^H = 2{,}77$; $a_4^H = a_6^H = 4{,}49$	—
2-Chloro-1,3-dinitrobenzene		12.2
4-Chloro-1,3-dinitrobenzene		10.7

Interesting correspondences have also been formed for nucleophilic reactions. The relative rates of substitution of chlorine in chloronitrobenzene under the influence of various nucleophiles agree satisfactorily with the constants a_i^H for the radical-anions. However, the treatment must be based on the values of a_i^H for the radical-anions of nitro-derivatives without chlorine. (The hyperfine interaction constants of the radical-anions of chloronitrobenzene and nitrobenzene are virtually the same.) Table 3 shows that the constant a_2^H (a_6^H)† of the radical-anion of 4-chloronitrobenzene is close to a_2^H (a_6^H) of the nitrobenzene radical-anion; exactly the same correspondence between the constants a_6^H and a_4^H is observed for the 2-chloronitrobenzene–nitrobenzene pair. Here $a_4^H > a_2^H$ in the nitrobenzene radical-anion. The substitution of the chlorine in 4-chloronitrobenzene by an ethoxy-group is easier and requires a smaller activation energy than the corresponding substitution in 2-chloronitrobenzene. The spin density in the 4-position of the 1,3-dinitrobenzene radical-anion is higher than in the 2-position $(a_4^H > a_2^H)$. The reactivity of 4-chloro-1,3-dinitrobenzene in nucleophilic substitution is correspondingly greater than that of 2-chloro-1,3-dinitrobenzene. The displacement of chlorine by the methoxide ion[16] in 4-chloro-3-methylnitrobenzene is faster than in 6-chloro-3-methylnitrobenzene (Table 4, Nos. 1 and 2) which agrees with the finding that the spin density in the 4-position of the 3-methylnitrobenzene radical-anion is greater than the 2-position[41] [cf. scheme (6)]. The same correspondence may be noted between the values of a_i^H for the 3-chloronitrobenzene radical-anion[39] [see scheme (6)] and the relative rate constants for the substitution by the methoxide ion[16] of the chlorine atoms at the *i*th carbon atoms (Table 4, Nos. 3 and 4).

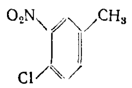
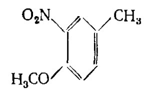
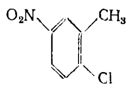
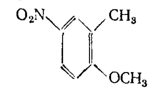
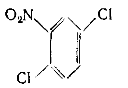
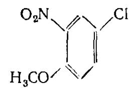
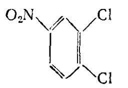
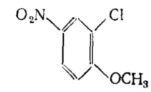


$a_6^H = 3.30$ G $a_4^H = 4.07$ G

$a_4^H = 3.88$ G $a_6^H = 3.20$ G

(6)

Table 4. The relative rate constants for the substitution of chlorine by a methoxide ion in certain chloronitrobenzenes in methanol at 25 °C.[16]

No.	Initial compound	Reaction product	k^{rel}
1			1
2			3.6
3			1
4			2.6

Thus the theoretical postulates described above support the possibility of the formation of substrate radical-ions and reagent radicals at the initial stage of the substitution reaction. There is evidence in support of a further combination of the radical-ion with the reagent radical or ion. The decomposition of the substrate radical-ion with formation of a secondary radical capable of interacting with another reagent molecule is also likely. Naturally, the agreement between the results of calculations and particular experimental data cannot by itself serve as proof that the one-electron transfer stage really occurs. For this, it is necessary to analyse the results of studies on the mechanisms of many specific reactions. Our discussion of theoretical problems was based on data for aromatic

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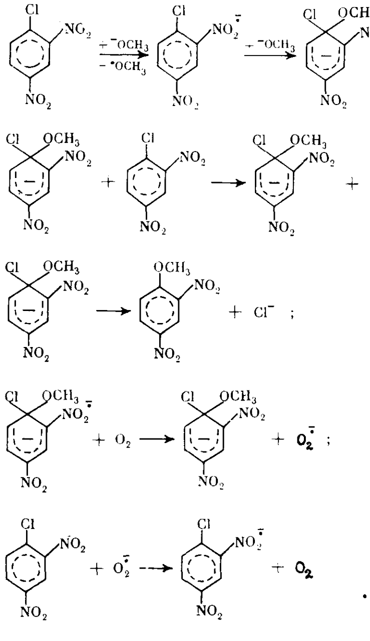
† The numbering of the positions in substituted nitrobenzenes begins with the atom linked to the nitro-group.

compounds: since the stability of aromatic radical-ions is high, they have been detected more frequently and more fully characterised. Thus, in considering specific reactions, we shall deal primarily with substitution in aromatic compounds.

IV. THE ROLE OF ONE-ELECTRON TRANSFER IN AROMATIC SUBSTITUTION REACTIONS

1. Nucleophilic Substitution

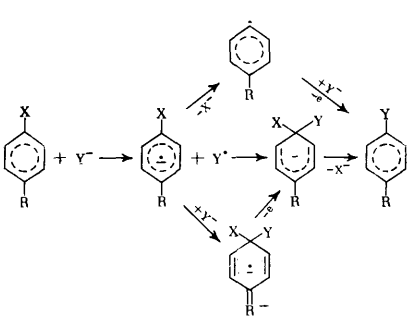
When 1-chloro-2,4-dinitrobenzene is treated with sodium methoxide, 2,4-dinitroanisole is formed. It has been established[42] that the reaction mixture contains the radical-anions of the starting material and the final product. Mechanism (7), which includes chain transfer steps involving electron exchange with participation of organic molecules and oxygen, has been put forward on the basis of ESR data for the accumulation and consumption of radical-anions[42]:



(7)

The catalytic effect of oxygen indicated by mechanism (7) agrees with the finding that nucleophilic reactions of aromatic nitro-compounds are an order of magnitude slower in nitrogen than in air. Benzoquinone or tetracyanoethylene inhibits such reaction; they are accelerated under the influence of light and are faster in glass apparatus than in cast iron apparatus[42]. All these findings support a radical mechanism of the reaction. An important feature of the mechanism of aromatic substitution reactions [mechanism (7)] is that it constitutes a harmonious combination of newly formulated concepts with earlier ideas, leading ultimately to a σ-complex as the usual precursor of the substitution product.

The radical-anion may not be converted into the substitution product solely via a radical-dianion as in scheme (7). The radical-anion may be converted into a free radical and then into the final product, bypassing the σ-complex. These possibilities are described in the scheme[42]



(8)

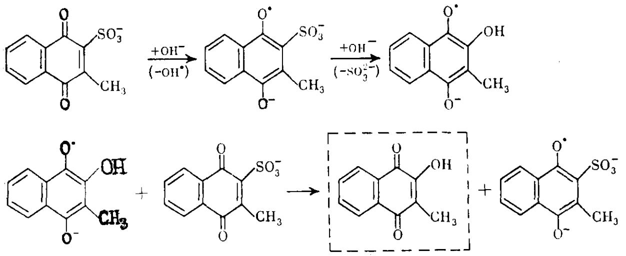
All the pathways taken into account in scheme (8) are based on the hypothesis of one-electron transfer with formation of a radical-ion. Apart from the data quoted above, the formation of the radical-anion is indicated by numerous kinetic studies[42]. The σ-complex obtained in the reaction exhibits the effect of chemically induced nuclear polarisation[43] (the CINP effect).

At the same time scheme (8) emphasises that the reactions of aromatic compounds with nucleophiles can proceed via different mechanisms with participation of various intermediate species. The contribution of each mechanism depends on the reaction conditions, including the effect of the structure and the medium. The same initial compounds may give rise to final products with identical structures via different mechanisms. This leads to the problem of estimating the contribution of a particular mechanism and the criterion should be the type of the rate-determining intermediate species rather than the reaction order. According to Shein[42], the classification of the mechanisms of the nucleophilic substitution reactions of aromatic compounds based on the reaction order, generally accepted at the present time, is inadequate. He suggested[42] that the mechanisms be classified in terms of the type of intermediate species: radical-ion, free-radical, carbanionic, etc. mechanisms. Reactions involving several species are also possible, for example, the process with a mechanism of the radical-ion–radical-dianion–σ-complex type indicated in scheme (7). The fundamental characteristics of scheme (7) have been attributed[42] to many other nucleophilic substitution reactions of aromatic compounds, including the substitution of chlorine by a methoxy-group in 4-chloronitrobenzene. In the latter case the formation of the main product is accompanied by that of a side product—4-nitrophenol (yield up to 15%). The ambiguity in the treatment of the pathways leading to the side product is striking. According to Shein's data[42], the main product (4-nitroanisole) is oxidised. Solodovnikov[44] justified a fundamentally different pathway—the oxidation of the radical-anions of the initial compound. The ambiguity of the treatment becomes of fundamental importance, because, according to Solodovnikov[44], virtually all 4-chloronitrobenzene radical-anions are converted into 4-nitrophenol. It was concluded on this basis that the "formation of 4-chloronitrobenzene radical-anions is a reaction taking place simultaneously with the substitution reaction"[44]. If this conclusion is accepted, one must assume that the substitution reaction itself proceeds either via a non-radical mechanism or via cryptoradical mechanism, where radical species are formed and combined in a solvent "cage" without emerging into the solution. It is so far difficult to make a choice between Shein's[42] and Solodovnikov's[44] treatments.

There is a greater unanimity in the treatment of the mechanism of another nucleophilic reaction—the substitution of a nitro-group in 1,2-dinitrobenzene (DNB) by a hydroxy-group. Various investigators have established the following facts: (1) that the reaction of DNB with OH^- ion in aqueous dimethyl sulphoxide results in the formation of 2-nitrophenoxide and nitrite only[45]; (2) that a long-lived DNB radical-anion is formed on mixing the reactants[45,46]; (3) that in the system considered the electron donor is indeed the OH^- ion, which is converted into the short-lived $OH^{\cdot}$ radical[46]; (4) that a σ-complex containing an OH group at the tetrahedral carbon atom is formed in the pathway to 2-nitrophenoxide[45]; (5) that the initial DNB and the σ-complex are not involved in electron exchange with one another[45]; (6) that the reaction of DNB with $O_2^{\overline{\cdot}}$ also leads to the substitution of the nitro-group by a hydroxyl and that DNB forms a radical-anion[47]; (7) that in the interaction of DNB with OH^- the one-electron transfer leading to the formation of the radical-anion takes place in the first stage with participation of uncharged DNB; [45] (8) that the kinetic curve for the accumulation and consumption of the DNB radical-anion is S-shaped and that the curve for the accumulation of 2-nitrophenoxide is parabolic (the start of the descending branch of the curve for the radical-anion corresponds to an inflection in the curve for the final product)[45]; (9) that kinetic calculations agree with experimental data only when the DNB radical-anion is regarded as the starting material in the substitution of a nitro-group by an OH^- ion[45].

A radical-ion mechanism has also been adopted[48] for the substitution of chlorine in 2-chloro-9,10-anthraquinone by a methoxy-group under the influence of sodium methoxide. The reaction represents a typical instance of substitution; during its course, 2-chloroanthraquinone radical-anions are formed, their number initially increasing to a maximum and then falling sharply. The addition of an inhibitor (benzo-1,4-quinone) lowers the rate of formation of radical-anions, which entails also a decrease of the rate of formation of 2-methoxyanthraquinone. If the radical-anions were obtained via a secondary pathway, the rate of formation of the final product should not have increased following the introduction of an inhibitor. It should have actually increased, since the oxidation of the radical-anions involves the regeneration of uncharged substrate molecules, which implies that the radical-ion mechanism is decisive in the given instance. Other nucleophilic reactions of anthraquinones are also associated with the formation of radical-anions: hydroxylation of 9,10-anthraquinone-2-sulphonic acid[48]; hydroxylation, alkoxylation or cyanation of the homoaromatic ring of 9,10-anthraquinone condensed in the 1,2-positions with the 2,1,5-oxadiazole ring[49]. However, the authors[48,49] adduce arguments according to which the one-electron reduction of the quinone takes place simultaneously with the main nucleophilic reaction. For example, it has been found that the concentration of anthraquinone-2-sulphonate radical-anions ceases to depend on the duration of the reaction with the alkali after a certain time interval and the overall yield of the radical-anion does not exceed 10%.[48] The introduction of inhibitors [oxygen, potassium hexacyanoferrate(III)] prevents the formation of radical-anions and the yield of 2-hydroxyanthraquinone actually increases somewhat[48]. In this case the radical-ion pathway in the process is not the main one.

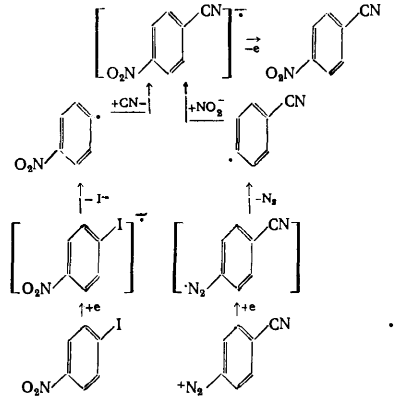
This example shows that the inclusion of the electron transfer stage in the reaction mechanism must be justified in each individual case. It is of interest that another representative of the class of quinone sulphonates—sodium 3-methyl-1,4-naphthoquinone-2-sulphonate—also gives rise to a radical-anion on reaction with alkali. The final product is 2-hydroxy-3-methyl-1,4-naphthoquinone. As the reaction proceeds, the number of radical-anions reaches a maximum and then falls immediately and at this instant the concentration of the final product begins to increase[48]. When inhibitors [oxygen, potassium hexacyanoferrate(III)] are introduced, neither the accumulation of radical-anions nor the formation of the final product is observed[48], which shows that the hydroxylation of 3-methyl-1,4-naphthoquinone-2-sulphonic acid proceeds via a radical-ion salt in accordance with the chain mechanism



(9)

etc.

The results concerning the "reconstruction" stages in the nucleophilic substitution of 4-iodonitrobenzene by a cyanide ion, quoted by Russell et al.[8], are of interest. One-electron reduction at an electrode in the presence of cyanide leads to the 4-iodonitrobenzene radical-anion. Like other halogeno-derivatives, 4-iodonitrobenzene readily splits off a halide ion in the radical-anionic state and is converted into a 4-nitrophenyl radical (a radical of the σ-electron type). The latter reacts with a cyanide ion and gives rise to a 4-cyanonitrobenzene radical-anion. The same radical-anion may be arrived at by reducing a 4-cyanobenzenediazonium salt with dithionite in the presence of nitrite. One-electron oxidation by the initial substrate converts the radical-anion into neutral 4-cyanonitrobenzene:



(10)

Singh and Kumar[50] obtained data showing that the substitution of a diazo-group linked to an aromatic compound by iodine also proceeds via an electron transfer stage. When arenediazonium fluoroborates are treated with potassium iodide in methanol (under nitrogen), iodobenzenes are formed:

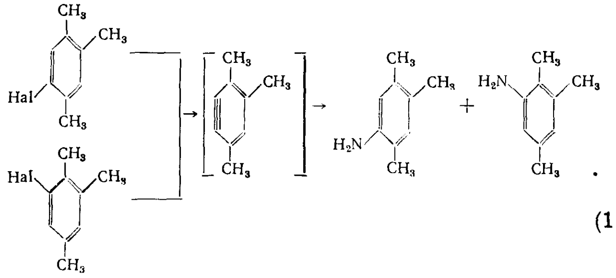
$$ArN_2^+ + I^- \longrightarrow ArN_2^{\cdot} + I^{\cdot};\quad I^{\cdot} \longrightarrow {}^1\!/_2 I_2;$$

$$ArN_2^{\cdot} \xrightarrow{-N_2} Ar^{\cdot};\quad Ar^{\cdot} + I^- \longrightarrow Ar{-}I^{\overline{\cdot}}; \tag{11}$$

$$ArI^{\overline{\cdot}} + ArN_2^+ \longrightarrow \boxed{ArI} + ArN_2^{\cdot} \text{ etc.}$$

Mechanism (11) is consistent with the known ability of the iodide ion to transfer one electron and also with the fact that the reaction is accelerated on irradiation with light and is inhibited in the presence of oxygen. In the presence of electron-accepting substituents in the benzene ring, the reaction rate increases, falling if electron-donating substituents are present. In the reaction involving 4-nitrobenzenediazonium, nitrobenzene, elemental iodine, and formaldehyde were found together with 4-iodonitrobenzene[50]. Formaldehyde is formed when 4-nitrophenyl radicals abstract hydrogen atoms from the solvent—methanol ($CH_3OH \rightarrow CH_2O$). Despite a careful search, neither 3-iodonitrobenzene nor 4-nitroanisole could be found among the products. This disproves another possible mechanism—cine-substitution involving the formation of dehydrobenzene.

The relation between cine-substitution and radical-ion mechanisms has been examined[51]. The reactions of 5- and 6-halogenopseudocumenes with potassium amide in liquid ammonia lead to 5- and 6-pseudocumidines, both isomeric amines being obtained regardless of whether the 5- or 6-position in the initial molecule contains a halogen atom. The nature of the halogen atom does not affect the ratio of the amino-derivatives obtained in the reaction of chloro- and bromo-derivatives; the ratio is constant and close to 1.5. The isomer ratio is not constant only for iodo-derivatives, being 0.63 and 5.86 when 5-iodopseudocumene and 6-iodopseudocumene are used respectively as starting materials. According to the authors[48], the cine-substitution mechanism is the only one in the reactions of chloro- and bromo-derivatives,



(12)

The reaction of iodopseudocumenes ArI proceeds not only via mechanism (12) but also via one-electron transfer:

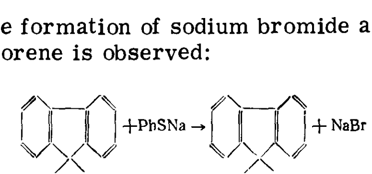
$$\mathrm{ArI} \longrightarrow (\mathrm{ArI})^{\overline{\cdot}} \longrightarrow \mathrm{Ar}^{\cdot} + \mathrm{I}^{-};$$

$$\mathrm{Ar}^{\cdot} + \mathrm{NH}_2^{-} \longrightarrow (\mathrm{ArNH}_2)^{\overline{\cdot}}; \qquad (13)$$

$$(\mathrm{ArNH}_2)^{\overline{\cdot}} + \mathrm{ArI} \longrightarrow \boxed{\mathrm{ArNH}_2} + (\mathrm{ArI})^{\overline{\cdot}} \text{ etc.}$$

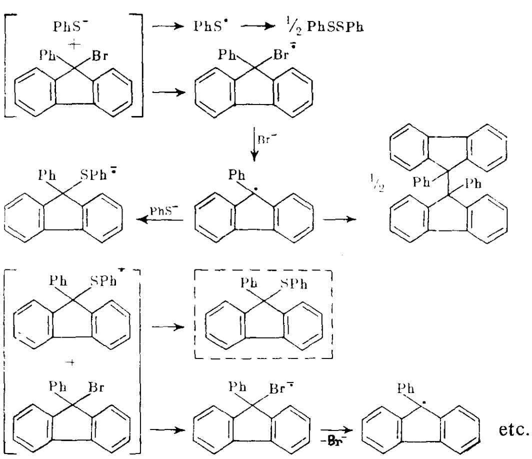
The hypothesis that mechanisms (12) and (13) operate simultaneously has been confirmed by experiments in the presence of radical-trapping agents: the introduction of 2-methyl-2-nitrosopropane or tetraphenylhydrazine alters the ratio of the pseudocumidines and makes it equal to 1.5 (for both 5- and 6-iodopseudocumenes). A characteristic feature of the iodopseudocumene radical-anions is that they split off a halide anion more readily than other halogeno-derivatives. As a result pathway (13), involving an electron transfer stage, becomes important.

The necessity to take into account the radical stage in nucleophilic substitution is also indicated by the results of a study of the mechanism of the introduction of an arylthio-group into 9-bromo-9-phenylfluorene[52]. When this bromo-derivative is treated with sodium thiophenoxide in dimethylformamide (DMF) in an atmosphere of nitrogen (30°C, 4 h), the formation of sodium bromide and 9-phenyl-9-phenylthiofluorene is observed:



(14)

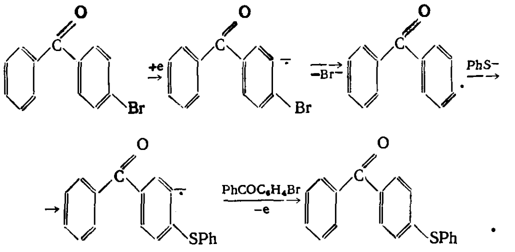
Sodium bromide is obtained quantitatively and the yield of the nucleophilic substitution product is only 42% of the theoretical value. The substrate and the nucleophile are also involved in other reactions which lead to 9,9-diphenylbifluorenyl (in 38% yield) and diphenyl disulphide (in 30% yield). The formation of these substances, which are indicated in scheme (15), conflicts with the usual ideas concerning nucleophilic substitution. Attention should be drawn to the fact that, in the presence of radical traps (oxygen and tetrabromo-*o*-benzoquinone), the formation of both the side products enumerated above and of the products resulting from the introduction of the arylthio-group is retarded[52]. Consequently the stage involving electron transfer from the nucleophile to the substrate occurs in the main reaction pathway, as in scheme (15). A phenylthiyl radical and a substrate radical-anion are formed in this stage. Both radical products are involved in further reactions: the phenylthiyl radical gives rise to diphenyl disulphide, while the substrate radical-anion is converted into a 9-fluorenyl radical. The latter reacts in two ways. It dimerises to bifluorenyl and, on reacting with a nucleophile, gives rise to a radical-anion of the "nucleophilic substitution product". Chain propagation is ensured by electron transfer from the above radical-anion to an unreacted substrate molecule, which loses a bromine atom and then reacts with the nucleophile, etc.



(15)

Mechanism (15) differs from mechanisms of the S_N1 or S_N2 type precisely by the inclusion of the one-electron oxidation-reduction stage. The driving force in this stage may be the ease of elimination of a bromide anion and the formation of a fluorenyl radical unsaturated in the 9-position, next to the stabilising benzene rings.

It has been shown[53] that the introduction of arylthio-groups into bromo-derivatives may be "stimulated" by creating conditions which promote the primary formation of radical-anions. Nucleophilic substitution of bromine by the thiophenoxide ion in 4-bromobenzophenone requires extremely severe conditions. When potentials are applied, the reaction proceeds readily and with a high yield (80%). It is sufficient to employ potentials which ensure solely the formation of substrate radical-anions (the potential and the amount of current passed through the system are strictly controlled). Next comes the chemical reaction in the bulk of the solution with formation of 4-phenylthiobenzophenone[53]:

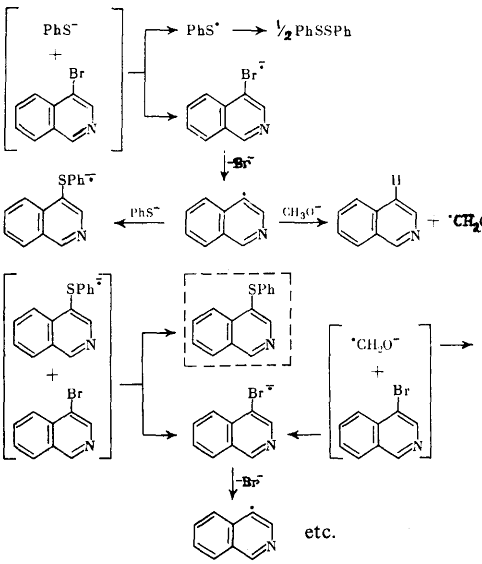


(16)

Nucleophilic substitution may be accelerated also without applying potentials, by introducing into the reaction mass substances which can behave as powerful electron donors. Thus sodium methoxide catalyses the introduction of an arylthio-group into 4-bromoisoquinoline by sodium thiophenoxide [scheme (17)].[54]

The introduction of sodium methoxide constitutes together with the introduction of thiophenoxide, yet another electron source for the generation of substrate radical-anions. However, if the thiophenoxide is converted into a phenylthiyl radical, as a result of electron transfer to the substrate, and then into the disulphide and is thus removed from the reaction sphere, substrate radical-ions are generated in the presence of methoxide ions with retention of a major proportion of the thiophenoxide. The overall rate of introduction of the arylthio-group in the presence of sodium methoxide increases and the yield of 4-phenylthioisoquinoline rises. However, the yield of side product—an unsubstituted isoquinoline—also increases with formation of only traces of the product of a competing substitution reaction—4-methoxyisoquinoline.

The introduction of azobenzene suppresses the effect of sodium methoxide, which confirms the radical-chain mechanism of the reactions via the scheme[54]:



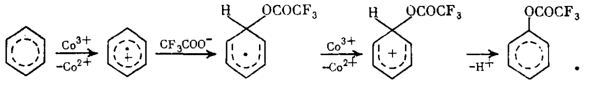
(17)

The formation of the phenylthiyl radical in reactions (15) and (16) was inferred from the isolation of diphenyl disulphide[52,64]. Bank and Noyd showed directly[55] that the phenylthioxide ion is involved in nucleophilic substitution and gives rise to a phenylthiyl radical. If styrene is added to a reaction mass containing 2-butyl nosylate (2-butyl 4-nitrobenzenesulphonate) as the substrate and sodium thiophenoxide as the reagent‡, the styrene polymerises with incorporation of phenylthiyl radicals. The corresponding sulphur-containing oligomer was isolated and characterised. When the thiophenoxide is mixed with styrene in the absence of the nosylate, the oligomer is not formed. When a radical trap (t-butyl phenyl nitrone) was introduced into the reaction mass, the reaction of 2-butyl nosylate with lithium thiophenoxide was retarded and the product of the addition of the phenylthiyl radical to the nitrone was detected by ESR. This indicates the formation of phenylthiyl radicals in the main pathway of the nucleophilic reaction.

2. Electrophilic Substitution

The study of the mechanisms of electrophilic substitution is extremely difficult, because aromatic radical-cations are much less stable than the radical-anions. Much less information has therefore been obtained about the role of one electron oxidation in the mechanisms of these reactions than for nucleophilic substitution in aromatic compounds.

Kochi et al. recently found a method of synthesising and stabilising radical-cations in trifluoroacetic acid, which consists in rapid mixing and freezing of solutions of the aromatic compound and thallium(III) or cobalt(III) trifluoroacetate[56]. When frozen solutions are heated, it is possible to observe well resolved ESR spectra of aromatic radical-cations. The latter are converted into aryl trifluoroacetates. It has been shown[56] that two oxidant molecules are consumed per molecule of the aromatic compound; the rate-limiting stage is one-electron oxidation with formation of a radical-cation. The reactions involving benzene can be represented as follows[56]:



(18)

The anodic acetoxylation of aromatic compounds in acetic acid solutions containing alkali metal or tetraalkylammonium acetates proceeds quite analogously to oxidative substitution [reaction (19)]. Investigations have shown[57] that the process begins with one-electron oxidation at the anode and is followed by the stages indicated in scheme (18). The reaction proceeds very readily also at potentials very remote from the oxidation potential of the acetate ion (+2.00 V relative to sat. c. e.)§. For example, the lowest anodic potential at which ring acetoxylation of anisole can be observed is 1.20 V.[57] The acetate ion in the final product originates from the acetate salt and not from acetic acid: when the acetate is replaced by tosylate or perchlorate with the same cation, the acetoxylation of anisole does not occur even when acetic acid is used as the solvent[57].

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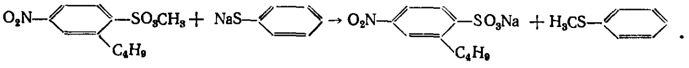
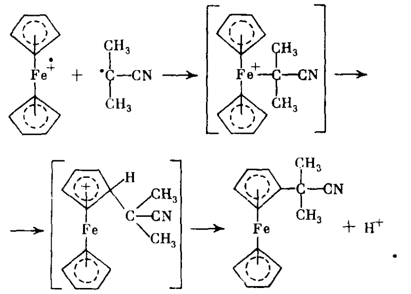
‡ The final result of this reaction can be represented schematically as follows:



$$O_2N{-}C_6H_4{-}SO_3CH_3(C_4H_9) + NaS{-}C_6H_5 \rightarrow O_2N{-}C_6H_4{-}SO_3Na + H_3CS{-}C_6H_5 \;(C_4H_9)$$

§ sat. c. e. = aqueous saturated calomel electrode.

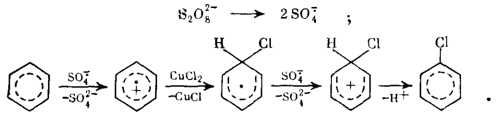
The radical-cation pathway in the substitution reaction is also illustrated in scheme (19).[58] In contrast to reaction (18), the radical-cation of the substrate interacts with a radical and not with an anion and the second one-electron oxidation stage is therefore not required in reaction (19):



(19)

The substitution product (α-cyanoisopropylferrocene) is formed in a yield up to 50% from ferrocene, copper fluoroborate, and azobisisobutyronitrile in acetonitrile at 80°C. In the absence of copper fluoroborate, which oxidises ferrocene to ferrocenium, the reaction does not occur, which implies that cyanopropyl radicals interact solely with ferrocenium and not with ferrocene. The product does not contain an unpaired electron and is therefore inert in relation to further substitution. This is an advantage of reaction (19) over Friedel-Crafts alkylation, in which products with an alkyl substituent undergo further substitution more readily than the initial ferrocene[58].

Copper(II) salts combine the properties of a one-electron oxidant[58] and a radical source[58, 59]. An interesting version of a radical-cation process is illustrated in the following scheme[59]:

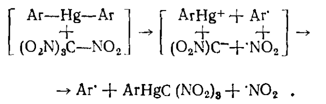


(20)

The reactions examined hitherto constitute instances of somewhat unusual substitution. They all proceed via a radical-ion pathway, because the substrate is introduced into the reaction after deliberate preliminary oxidation to the corresponding radical-cation. Studies on the mechanisms of the reactions which proceed as "typical" substitution processes without oxidation by an extraneous reagent are of interest. An example of "typical" substitution is the dark chlorination of benzene derivatives. In his study of the chlorination of toluene in acetic acid, Kochi[60] concluded that a toluene radical-cation is formed at an intermediate stage and that it reacts further with chlorine to give a chloro-derivative. The author bases this conclusion on the appearance of a well resolved ESR signal due to the radical-cation when acetic acid solutions of the substrate and chlorine are mixed directly in the spectrometer cell. Unfortunately, no data are quoted in his communication[60] concerning the kinetics of the accumulation and consumption of the radical-cation during the chlorination process and it is therefore impossible to decide whether the radical is formed in the main or a secondary reaction pathway.

However, one must emphasise that electrophilic substitution via electron transfer is promoted by two important factors[60]: aromatic molecules are oxidised at fairly low potentials; the electrophile (for example, a halogen) readily undergoes one-electron reduction. Similarly the nitronium ion, which is directly or indirectly involved in aromatic nitration, can be readily reduced to nitrogen dioxide[60].

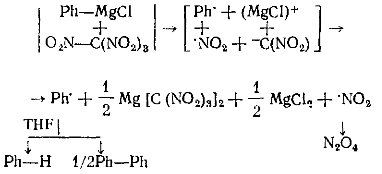
In our discussion of the nitration of benzene within the framework of scheme (2), we noted that, apart from the stage involving the formation of π- and σ-complexes, the interaction of benzene with the nitronium cation can also include an electron transfer stage. The σ-complex should then be obtained as a result of the combination of the benzene radical-cation and the $^{\cdot}NO_2$ radical. The decomposition of the σ-complex leads to nitrobenzene. If the decomposition is rapid, occurring over a period up to 10 s, the resulting nitrobenzene should give rise to a CINP effect. However, the effect could not be observed[61], although according to ^1H NMR data the reaction was not arrested appreciably in the σ-complex formation stage. Thus the electron transfer stage in reaction (2) was not confirmed experimentally. However, one should note that this stage may be unfavourable precisely for the nitration reaction owing to the low reactivity of the $^{\cdot}NO_2$ radical in the liquid phase. This idea is suggested by the results of a study of the interaction of aryl derivatives of tin, magnesium, and mercury with tetranitromethane in sulpholane[62]. For example, in the reaction of diarylmercury with tetranitromethane[62], the aryl and $^{\cdot}NO_2$ radicals are formed in an intermediate stage [see scheme (21)]. Despite the high reactivity of the aryl radical, it is scarcely attacked by the $^{\cdot}NO_2$ radical and gives rise mainly to an aromatic hydro-carbon as a result of reaction with the solvent. The trinitromethyl anion combines with the arylmercury cation, while the $^{\cdot}NO_2$ radical is probably stabilised in the form of nitrogen tetroxide and is subsequently consumed in secondary oxidation reactions:



$$\left[\begin{array}{c} Ar{-}Hg{-}Ar \\ + \\ (O_2N)_3C{-}NO_2 \end{array}\right] \rightarrow \left[\begin{array}{c} ArHg^+ + Ar^{\cdot} \\ + \qquad + \\ (O_2N)C^- + {}^{\cdot}NO_2 \end{array}\right] \rightarrow$$

$$\rightarrow Ar^{\cdot} + ArHgC(NO_2)_3 + {}^{\cdot}NO_2 \quad . \qquad (21)$$

The amount of ionic character of the carbon–metal bond affects the ease of the electron transfer reaction. Whereas tetranitromethane reacts with aryl derivatives of mercury and tin only after heating for many hours at 80°C, the reaction with phenylmagnesium chloride occurs after mixing the reactants and requires a reduced temperature (−50°C). However, the overall result of the reaction is independent of the nature of the carbon–metal bond: in each of the instances considered, tetranitromethane does not play its characteristic role of a nitrating agent. Only traces of nitrobenzene are formed and the main organic product is benzene. In the reaction with phenylmagnesium chloride, biphenyl (in 20% yield) is formed together with benzene (in 55% yield); tetranitromethane gives rise to the magnesium salt of trinitromethane under these conditions (in 80% yield):



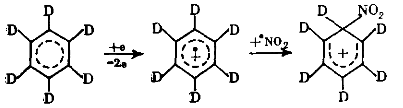
$$\left|\begin{array}{c} Ph{-}MgCl \\ + \\ O_2N{-}C(NO_2)_3 \end{array}\right| \rightarrow \left[\begin{array}{c} Ph^{\cdot} + (MgCl)^+ \\ + \qquad + \\ {}^{\cdot}NO_2 + {}^-C(NO_2) \end{array}\right] \rightarrow$$

$$\rightarrow \underset{\underset{Ph{-}H \quad 1/2Ph{-}Ph}{\downarrow\ THF}}{Ph^{\cdot}} + \frac{1}{2}Mg[C(NO_2)_3]_2 + \frac{1}{2}MgCl_2 + \underset{\underset{N_2O_4}{\downarrow}}{{}^{\cdot}NO_2} \quad . \qquad (22)$$

Nitrogen tetroxide is known to react with phenyl magnesium chloride[62]. However, reaction (22) is so rapid that the nitrogen tetroxide evolved has insufficient time to react with the initial phenylmagnesium chloride and impair the agreement, noted above, between the yields of the electron donor and acceptor conversion products. The authors[62] attribute the formation of biphenyl in reaction (22) to the oxidation of the dimeric form of phenylmagnesium chloride. The possibility of the recombination of phenyl radicals after their emergence from the cage is rejected[62] on the grounds that biphenyl is not formed in the reactions with Ph_2Hg and Ph_4Sn. The main result of the reaction of tetranitromethane with aryl derivatives of mercury, tin, and magnesium is the generation of $Ar^\cdot$ and $^\cdot NO_2$ radicals, which hardly interact with one another in the liquid phase.

In the gas phase the $^\cdot NO_2$ radical may acquire the needed reactivity. This is indicated by the ion–cyclotron resonance data analysed below[63]. Perdeuterobenzene and nitrogen tetroxide were admitted into the mass spectrometer chamber, whereupon the $(C_6D_6NO_2)^+$ ion, corresponding to the product of the addition of the nitro-group to perdeuterobenzene without the displacement of deuterium, i.e. a σ-complex, was detected. The authors[63] used double resonance in order to determine the species on the energy of which depends the rate of formation of the σ-complex. It was found that the rate depends unambiguously on the energy of the $C_6D_6^{\dotplus}$ radical-cations and is independent of the energy of the $^+NO_2$ cations[63]. This implies that the $C_6D_6^{\dotplus}$ and $^\cdot NO_2$ species, and not C_6D_6 and $^+NO_2$, are the precursors of the σ-complex:

$$N_2O_4 \longrightarrow 2\,^\cdot NO_2\ ;$$



(23) .

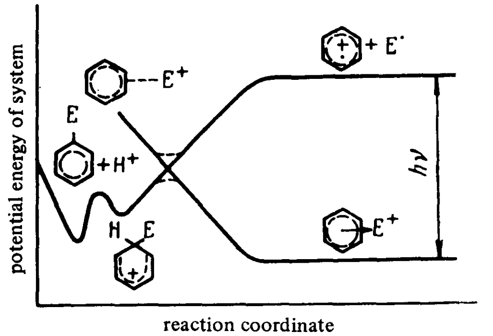


Figure 6. Variation of the potential energy in the substitution of benzene by an electrophile (E^+).

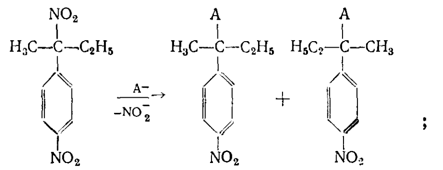
It has been noted[64] that one-electron transfer is a possible but not necessarily a discrete stage of the reaction involving substitution in aromatic compounds. We shall now consider how the potential energy of the system varies during the substitution. Fig. 6 illustrates such variation for electrophilic substitution in an aromatic compound[20]. Before the start of the reaction, the potential energy of the system is a maximum; a decrease of this energy is observed when a π-complex is formed. The separation (transfer) of the single charge in the π-complex leads to a readical-cation of the aromatic compound and an electrophile radical. The energy increases by *hν*, and the system acquires a different energy profile. The quantity *hν* determines the probability of the electron transfer stage. The radical-ion–radical pair ($C_6H_6^{\dotplus} + E^\cdot$) can rearrange into a σ-complex, which corresponds to a well in the new energy profile. The further decrease of energy is attributed to the formation of an electrophilic substitution product and the elimination of a proton. The energy curves cannot intersect. A gap, bounded by dashed semicircles, arises. It is small, which ensures the possibility of a transition from one curve to the other. In other words, the reaction may proceed via the pathway involving reverse electron transfer from $E^\cdot$ to $C_6H_6^{\dotplus}$ with return to the initial state. The initial compounds (benzene and the electrophile) then give rise to π- and σ-complexes along the pathway to the final product without forming radical species in the intervening stages.

The radical stage becomes more probable when the energy gap *hν* becomes sufficiently narrow to be overcome as a result of collision energy or under the conditions of a more favourable organisation of the solvation shell. The gap *hν* is more easily overcome in interactions which lead to relatively stable electron transfer products or when these products decompose into rapidly and irreversibly reacting species. The gap can be easily overcome when there is a considerable difference between the oxidation-reduction potentials of the substrate and the reagent (in other words, between their LUMO and HOMO levels). In certain cases the distance *hν* can be crossed with the aid of external influences: by the application of potentials, by the introduction of a stronger donor or acceptor, by irradiation, and by initiation with participation of a third molecule (a donor, or an acceptor, or a solvent).

Naturally, the above factors should promote the electron transfer stage not only in substitution reactions of aromatic compounds but also in substitution reactions involving a series of aliphatic compounds.

V. ONE-ELECTRON TRANSFER IN ALIPHATIC SUBSTITUTION REACTIONS

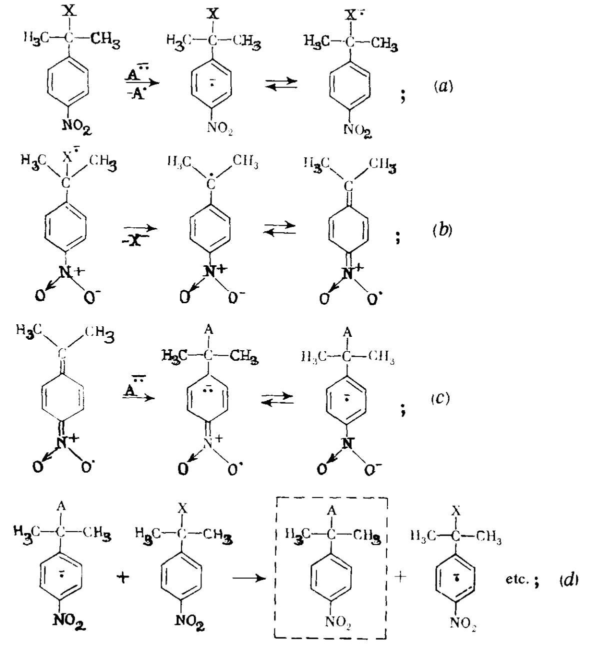
Among the first studies dealing with the radical stages in the mechanism of substitution reactions of aliphatic compounds, those of Kornblum's school[7] occupy an important place. In his studies of substitution at a saturated tertiary carbon atom Kornblum compared the behaviour of α-cumenyl chloride, α-nitrocumene, and their 4-nitro-derivatives in relation to anions. It was found that only the cumenyl compounds containing the nitro-group in the 4-position undergo substitution in the α-position. The reaction proceeds equally well with small and bulky anions. Such insensitivity to steric hindrance makes it possible to obtain highly branched products. When 4-nitrocumenyl chloride is treated with sodium thiophenoxide in argon or in nitrogen, two products are formed: 4-nitro-α-phenylthiocumene and 4,4′-dinitrobicumenyl. It is remarkable that, on reacting with sodium thiophenoxide, the optically active substrate gives rise to a racemic substitution product. Racemisation is observed also on treatment with sodium nitrite [scheme (24)]. In the presence of nitroxy-radicals or aromatic nitro-compounds, the substitution reaction is suppressed. Oxygen sharply retards the formation of substitution products, but promotes the formation of 4-nitrocumenyl hydroperoxide. Illumination has a marked initiating influence:



(24)

$A = C_6H_5S$, or NO_2.

The above findings fit logically within scheme (25), where a dual role is attributed to the anion A^-: that of an electron donor [stage (*a*)] and of the species undergoing addition [stage (*c*)]:



(25)

$A = C_6H_5S$ or NO_2; $X = Cl, N_3, C_6H_5SO_2, NO_2$, or OAr.

Scheme (25) explains two characteristics of the reaction: its applicability to 4-nitro-substituted substrates alone and its insensitivity to steric factors. The presence of the nitro-group in the 4-position ensures the delocalisation of the excess electron and thus promotes the formation of the radical-anion [stage (*a*)]. Stage (*a*) involves the unhindered aromatic nitro-fragment of the 4-nitrocumenyl system. Stage (*b*) consists of intramolecular elimination and is likewise not controlled by steric factors. Stage (*c*) includes the addition of the anion A^- to the planar system of the free radical. The free radical exhibits a high reactivity and is susceptible to attack by the anion. Consequently stage (*c*) may be rapid; this is important, because stage (*c*) propagates the chain of reactions (25). Chain branching takes place in stage (*d*), where the radical-anion of the substitution product transfers one electron to an uncharged substrate molecule. The one-electron transfer at this stage proceeds as in other cases, rapidly and independently of steric factors[7]. As a result, substitution at the strongly hindered carbon atom involves a sequence of stages which is as a whole distinguished by a low sensitivity to steric effects. The ease of reaction (25) depends on the ease with which the anion A^- gives up an electron to the 4-nitrocumenyl system and thereby initiates the chain of stages (*a*)–(*d*).

If the above sequence of transformations takes place and stage (*c*) is indeed rapid and irreversible, such behaviour can be used to extend the limits of applicability of the reaction. The possibility arises of obtaining substitution products also with anions which do not enter into the reaction or react extremely slowly. The point is that the nitrocumenyl radical can be captured not only by the anions some of which have been used to generate this radical but also by other anions. A catalytic amount of a reactive nucleophile may induce the reaction of a less reactive (or completely inert) nucleophile with 4-nitrocumenyl chloride and α,4-dinitrocumene. This prediction, made by Kornblum, proved to be fully justified[7]. In the absence of elimination, sodium azide and α,4-dinitrocumene do not react (control time—48 h). In contrast to sodium azide, the lithium salt of 2-nitropropane reacts with α,4-dinitrocumene in the dark and after three hours gives the α-substitution product in 87% yield. If α,4-dinitrocumene (1 mole) is treated with sodium azide (2 moles) in the presence of the lithium salt of 2-nitropropane (0.1 mole), the entire initial α,4-dinitrocumene is converted in the absence of illumination over a period of 3 h into pure 4-nitrocumenyl azide in 97% yield. Such "stimulation" of the reaction has been observed also for the nitrocumenylchloride–sodium nitrite pair. Typical one-electron donors such as sodionaphthalene have been used successfully as "stimulating" agents[7].

According to Russell et al.[8] the substitution reactions in the series of α-x-α-nitroalkanes also involve a stage in which nitro-radical-anions are formed. The lithium salt of 2-nitropropane has also been used in this reaction as an electron donor. The formation of 2,3-dimethyl-2,3-dinitrobutane is accelerated under the influence of light; oxygen, dinitrobenzene, and free radicals have an inhibiting effect. The reactions have been described by the following scheme[8]:

$$(CH_3)_2C(NO_2)^- Li^+ + (CH_3)_2C(NO_2)X \longrightarrow (CH_3)_2\dot{C}(NO_2) + (CH_3)_2C(NO_2)X^{\dot{-}}\,Li^+;$$

$$(CH_3)_2C(NO_2)X^{\dot{-}}Li^+ \longrightarrow (CH_3)_2\dot{C}(NO_2) + LiX;$$

$$(CH_3)_2\dot{C}(NO_2) + (CH_3)_2C(NO_2)^-Li^+ \longrightarrow (CH_3)_2C(NO_2)C(CH_3)_2(NO_2)^{\dot{-}}Li^+; \qquad (26)$$

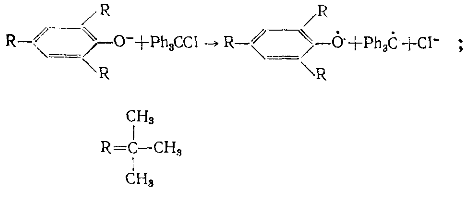
$$(CH_3)_2C(NO_2)C(CH_3)_2(NO_2)^{\dot{-}}Li^+ + (CH_3)_2C(NO_2)X \longrightarrow$$

$$\longrightarrow \boxed{(CH_3)_2C(NO_2)C(CH_3)_2NO_2} + (CH_3)_2C(NO_2)X^{\dot{-}}Li^+ \text{ etc.}$$

$X = Cl, CN$, or NO_2.

Mechanism (26) has been extended to a large series of practically important reactions of 2,2-dinitropropane and 2-bromo-2-nitropropane with other carbanions[8].

The kinetics of the electron transfer stage in nucleophilic substitution at a saturated carbon atom have been investigated[65,66] and model systems in which stable free radicals are formed in the reactions have been examined. This enabled the author to investigate the kinetics of electron transfer on the basis of the accumulation of the radicals. The interaction of triphenylmethyl chloride with a sterically hindered phenoxide in accordance with the scheme



(27)

was chosen as a model of nucleophilic substitution. The model was justified in the following way.

"Since nucleophilic substitution involves the replacement of one anion by another and the electron may be regarded as the simplest nucleophile, the very formation of radicals in reaction (27) constitutes in essence the simplest type of nucleophilic substitution of a halogen by an electron"[66]. The initial rate of accumulation of phenoxy-radicals is related to the phenoxide and triphenylmethyl chloride concentrations by the equation

$$w_0 = \left.\frac{d\,[\mathrm{Ar\dot{O}}]}{dt}\right|_{t\to 0} = k_1\,[\mathrm{Ph_3CCl}] + k_2\,[\mathrm{Ph_3CCl}]\,[\mathrm{ArOK}]^2 \qquad (28)$$

where the constant k_1 describes the rate of dissociation of Ph_3CCl into ions, the first term of the equation being independent of the concentration [ArOK]. The authors[9, 65, 66] believe that this term corresponds to the reaction of the ionised triphenylmethyl chloride or the free triphenylmethyl cation with the phenoxide:

$$\begin{aligned} &\mathrm{Ph_3CCl} \rightleftarrows \mathrm{Ph_3C^+} + \mathrm{Cl^-} \quad ; \\ &\mathrm{Ph_3C^+} + {}^{-}\mathrm{OAr} \rightarrow \mathrm{Ph_3\dot{C}} + {}^{\cdot}\mathrm{OAr} \quad . \end{aligned} \qquad (29)$$

The second term of Eqn. (28), which is quadratic in the phenoxide concentration, corresponds to electron transfer on collision of three molecules when the reaction involves undissociated triphenylmethyl chloride:

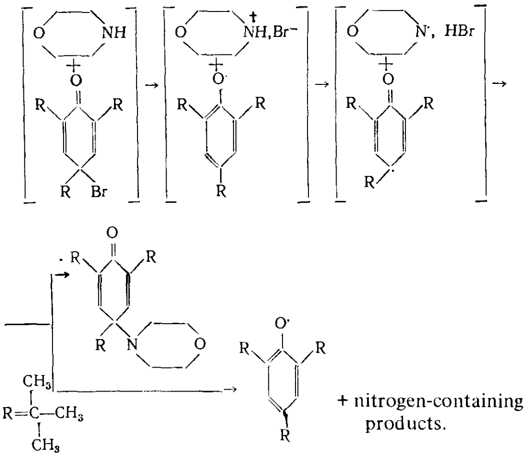
$$\mathrm{ArO^-} \ldots\ldots \mathrm{Ph_3CCl} \ldots\ldots \mathrm{MOAr} \rightarrow \mathrm{ArO^{\cdot}} + \mathrm{Ph_3C^{\cdot}} + \mathrm{Cl^-} \ldots\ldots \mathrm{MOAr} \ . \qquad (30)$$

The contribution of reactions (29) and (30) is determined by the solvating capacity of the solvent. When tetrahydrofuran (THF) is replaced by dimethoxyethane (DME), the contribution of reaction (29) increases almost by a factor of 2. In DMF only reaction (29) takes place, while in heptane reaction (30) occurs exclusively. The kinetic characteristics of the above model reaction have also been observed in the "typical" nucleophilic substitution of the halogen in alkyl halides by an alkoxy-group. In solvents of low polarity such reactions are frequently of third order overall (of first order with respect to the alkyl halide and of second order with respect to the alkoxide), but in highly polar solvents the reaction may be of first order with respect to the alkyl halide and of zero order with respect to the alkoxide. In solvents of moderate polarity there is a possibility of the simultaneous occurrence of the first- and third-order reactions[9, 65, 66]. On the basis of the kinetic study of electron transfer from the phenoxide to triphenylmethyl chloride, the authors[9, 66] suggest that the alcoholysis of alkyl halides be regarded as an oxidation-reduction reaction in accordance with the schemes below:

$$\begin{aligned} &\mathrm{RX} \rightleftarrows \mathrm{R^+} + \mathrm{X^-};\ \mathrm{R'O^-} + \mathrm{R^+} \rightarrow [\mathrm{R'O^{\cdot}} + \mathrm{R^{\cdot}}] \rightarrow \mathrm{R'OR}\ ; \\ &\mathrm{R'O^-} \ldots\ldots \mathrm{R{-}X} \ldots\ldots \mathrm{MOR} \rightarrow [\mathrm{R'O^{\cdot}} + \mathrm{R^{\cdot}}] + \mathrm{X^-} \ldots\ldots \mathrm{MOR}; \end{aligned} \qquad (31)$$

$$[\mathrm{R'O^{\cdot}} + \mathrm{R^{\cdot}}] \rightarrow \mathrm{R'OR} \quad . \qquad (32)$$

These schemes represent a generalisation based on the results of studies of the model reaction which stops at the stage involving the formation of radical species incapable of combining with one another[¶]. The study of the amination of quinobromides undertaken by Bubnov[66], in which the liberation of radicals from the cage is accompanied by their combination with formation of the final S_N2 substitution products, is therefore of fundamental importance. When morpholine is used as the amine, the degree of liberation of the radicals from the cage is ~10% (according to ESR data). This implies that 90% remains as the contribution of the substitution process. Indeed the yield of quinamines in the syntheses proved to be 85%. The entirely satisfactory agreement between the yield of the reaction product estimated from kinetic ESR data and from independent chemical data may be regarded as part of the evidence in support of the following scheme:

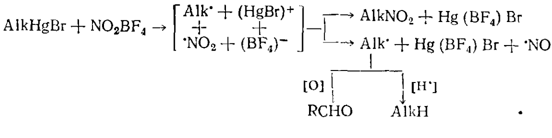


(33)

The electrophilic substitution reaction[67]

$$\mathrm{AlkHgBr} + \mathrm{NO_2BF_4} \rightarrow \mathrm{AlkNO_2} + \mathrm{Hg\,(BF_4)\,Br} \qquad (34)$$

also proceeds as an oxidation-reduction process. The yield of the nitro-derivative in this process is low; in addition, an aliphatic hydrocarbon and an aldehyde are obtained. The authors explain these features of the process by mechanism (35), which involves the intermediate formation of a radical-cation from alkylmercury bromide. The latter gives rise to a highly reactive alkyl radical. The nitronium cation captures an electron and is converted into the ·NO radical. The latter is relatively inactive [cf. schemes (22) and (23)]. For this reason, the reaction of alkyl radicals with nitrogen dioxide proceeds to only a slight extent, a considerable proportion of the radical emerging from the cage into the bulk of the solution. Nitrogen dioxide radicals are probably consumed in secondary oxidation reactions and alkyl radicals either split off hydrogen from the solvent and form a hydrocarbon or are oxidised and give rise to an aldehyde[67]:



$$\mathrm{AlkHgBr} + \mathrm{NO_2BF_4} \rightarrow \begin{bmatrix} \mathrm{Alk^{\cdot}} + (\mathrm{HgBr})^+ \\ + \qquad + \\ {}^{\cdot}\mathrm{NO_2} + (\mathrm{BF_4})^- \end{bmatrix} \rightarrow \begin{cases} \mathrm{AlkNO_2} + \mathrm{Hg\,(BF_4)\,Br} \\ \mathrm{Alk^{\cdot}} + \mathrm{Hg\,(BF_4)\,Br} + {}^{\cdot}\mathrm{NO_2} \\ \quad \xrightarrow{[\mathrm{O}]} \mathrm{RCHO} \qquad \xrightarrow{[\mathrm{H^{\cdot}}]} \mathrm{AlkH} \end{cases} \qquad (35)$$

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The above data show that the one-electron transfer stage is both possible and frequently observed in the mechanisms of substitution reactions. At the same time it is evident that there is no justification for applying the hypothesis of one-electron transfer to all cases without exception. In each specific reaction the one-electron

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[¶] The question of the validity of this generalisation gave rise to a controversy. It was emphasised that the formation of radicals only as the final products makes the reaction too different from other nucleophilic substitution reactions and actually necessitates "its classification as not an S_N reaction, but as an oxidation-reduction process"[10].

transfer stage requires experimental proof. The development of such studies is urgently required because it leads to the synthesis of the required final products or to an increase of their yield and of the rate of their formation. The main problem is to determine the subsequent fate of the species arising after the one-electron transfer. These species may undergo transformations of the $S_{RN}1$ or S_N2 type along the pathway to the final product. Transformations which take place via complexes containing a tetrahedral carbon atom belong to reactions of the S_N2 type. The complexes may be obtained both as a result of recombination in the biradical pair and after emergence from the solvent "cage" with subsequent attack by a further molecule of the reagent. Reactions of the $S_{RN}1$ type involve the elimination of the ionogenic group from the primary radical-ion and the subsequent addition of the reagent at the site of the free valence.

The possibility of recombination in the biradical pair is difficult to test and data characterising reactions of this type are still ambiguous. This has given rise to a sceptical[10] and sometimes extremely negative[68] assessment of the one-electron transfer hypothesis. Reactions involving the liberation of a radical-ion from the solvent "cage" or the formation of secondary radicals are more readily susceptible to investigation. This field is now attracting much attention and has already yielded results which are of both theoretical and practical importance.

Further development of such research requires, however, the solution of many more fundamental problems. It is necessary to know the difference between the oxidation-reduction potentials of the reagent and the substrate established under reaction conditions. It is necessary to discover the features which determine the state of equilibrium in electron transfer reactions. An important factor is the stability of the species formed on electron transfer. It is therefore essential to discover what factors promote the stabilisation and destabilisation of such species and what general changes in reactivity accompany the transition of the substance to the radical-ion state. All these problems are new to organic chemistry. The principal obscurities are associated with the insufficiency of information about the nature of the chemical behaviour of radical-ions. At the present stage the development of studies devoted to the role of the oxidation-reduction stages in the reaction mechanism depends on the level of our knowledge concerning the transformation of a given substance as a result of electron transfer.

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The Problem of Tetrahedrane

N.S.Zefirov, A.S.Koz'min, and A.V.Abramenkov

The theoretical and experimental studies on tetrahedrane—a highly strained compound—are surveyed. The bibliography includes 87 references.

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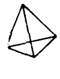
III. Experimental approaches to the synthesis of tetrahedrane 166

I. INTRODUCTION

After Baeyer proposed his "strain" theory based on simple geometrical considerations, organic chemists devoted much experimental labour, perseverance, and intellectual effort to the synthesis of highly strained structures. Purely geometrical approaches frequently serve as a starting point in the synthesis of skeletal and polycyclic compounds. It is sufficient to point out as an example the synthetic research in the field of tri- and penta-prismanes and related structures[1-5], propellanes[6], cubane[7-9], homotetrahedrane[10,11], dodecahedrane[12-14], etc., let alone the thoroughly developed field of the chemistry of adamantane[15], its heterologues[16], and higher derivatives ("adamantalogues")[17,18]. The fact that polyhedranes with a high symmetry are aesthetically attractive is itself a sufficient stimulus for "molecular design"[19]. However, the continued attention devoted by chemists to skeletal and polyhedral structures is naturally not due solely to abstract interest; these compounds frequently possess surprising properties, which makes their synthesis of interest from both theoretical and practical points of view. In particular, the chemistry of adamantane provides numerous examples of this. We may note here the problem of "molecular strain"[20], the dependence of the bond properties on the distortion of valence angles (for example, $J_{^{13}C-H}$ and the change in hybridisation), the stereochemistry of the inductive effect[22-24], etc., which have been examined using skeletal and polyhedral structures as models.

Organic molecules belonging to the T_d symmetry point group, the simplest of which is tetrahedrane (I), are of special interest in this respect.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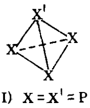
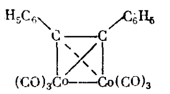


(II) X = X' = P
(III) X = X' = BCl
(IV) X' = CH₃C, X = B(C₂H₅)₃
(V) X' = RC, X = Co(CO)₃



(VI)

From the topological point of view, this molecule is interesting because its hydrocarbon skeleton constitutes the simplest connected cubic graph[25]. The very marked distortion of all the valence angles in the molecule should lead to enormous strain, which apparently reaches its limiting value for an organic molecule. We may also formulate several problems which make the task of synthesising tetrahedrane structures exceptionally urgent. The enormous strain in the tetrahedrane molecule should lead to a unique reactivity of the σ-bonds. Examples of a sharp change in the electronic structure of a formally single bond owing to strain, as, for example, in certain propellanes[6] and dehydroadamantane[26], are known in the literature. This property should be particularly striking in the tetrahedrane molecule. Another problem is associated with the study of the optical activity of structures having tetrahedral symmetry but no chiral centre. This problem has also been considered in relation to adamantane derivatives[27-29]. Finally heterotetrahedranes, in which new specific problems arise, such as that of the basicity of the heteroatom (nitrogen, phosphorus), complex formation, etc., might also be of considerable interest.

We may note that non-carbon tetrahedral structures, which may be assigned at least formally to heterotetrahedranes, have now been described. The simplest heterotetrahedrane is the P_4 molecule (II).[30] Tetrahedral structures are known for boron derivatives, for example (III)[31] and (IV)[32]. The cobalt clusters (V)[33] or (VI)[34] have the molecular topological form of tetrahedrane†.

However, the synthesis of the tetrahedrane carbon skeleton is of greatest interest. There is as yet no clear-cut description of the synthesis of tetrahedrane and only indirect evidence is available for the existence of molecules of this type. Nevertheless the literature devoted to this problem is fairly extensive and, bearing in mind the enormous fundamental importance of the problem, we thought it is useful to survey it, noting both theoretical and experimental advances.

II. THEORETICAL STUDY OF TETRAHEDRANE

As stated above, tetrahedrane is the most strained system among all possible saturated compounds containing

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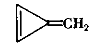
†This concept was introduced by one of the present authors (N.S.Zefirov) and by V.N.Drozd, V.I.Sokolov, and I.V.Stankevich. By the term molecular topological form, we understand the figure in the usual sense of the word plus certain singular points (atoms within the figure, the centre of inversion). For example, the molecular topological form for tetrasubstituted methane is a tetrahedron with a single singular point, while for hexasubstituted ethane it is an octahedron with two singular points. This concept serves as a basis for the definition of the most important stereochemical concept—that of configuration (configuration is the stereochemical equivalent of the topological form of the molecule). For the tetrahedron molecules considered in this study, the molecular topological form is a tetrahedron without internal points.

three-membered rings. The angular geometrical parameters of this molecule are fully determined by its symmetry and only the C–C and C–H distances can vary independently. Comparison of the geometry of tetrahedrane with that of bicyclo[1,1,0]butane shows that the dihedral angle between the three-membered rings in the latter is close to 126°, whilst in the tetrahedrane the corresponding angle should be 70°32'.[35] In this connection the problem arises of the thermodynamic stability of tetrahedrane in relation to the family of the isomeric C_4H_4 structure. Among these, we may note structures with closed shells such as those of methylenecyclopropene (VII), vinylacetylene (VIII), and cyclobutadiene (IX)‡. However, the main factor which determines the possibility of the existence of an isolated tetrahedrane molecule is the form of the potential energy hypersurface for the C_4H_4 system (in particular the presence of a minimum at the point corresponding to the tetrahedral configuration and the size of the potential barriers separating tetrahedrane from its possible conversion products).


(VII)

$CH_2{=}CH{-}C{\equiv}CH$

(VIII)


(IX)


(X)

Apart from the structures enumerated above, the system comprising two acetylene molecules and the biradical (X), obtained from tetrahedrane following the dissociation of a single C–C bond, may be assigned to systems of this kind. Regardless of thermodynamic stability, in the presence of large potential barriers the tetrahedrane molecule might exist as a long-lived metastable species. The most important theoretical study of the present problem is therefore that of the potential energy of the C_4H_4 system as a function of the geometrical configuration of the nuclear skeleton.

1. Investigation of the Potential Energy Surface for the C_4H_4 System

Since the geometry of the C_4H_4 system is determined by eighteen independent variables (geometrical parameters), the potential energy can be represented by a hypersurface in a 19-dimensional space. A quantum-mechanical calculation even for a small section of such a hypersurface is impossible in the present state of computing technique. By virtue of these factors, theoretical estimates of the energies of individual isomers with specified geometries are easiest at the present time. Calculations of the total energies of various isomers having the formula C_4H_4 and their estimation from thermodynamic characteristics have been made within the framework of semiempirical molecular orbital methods[36,38–40]; non-empirical quantum-mechanical calculations have become possible recently[37,41–43].

The relative distribution of the C_4H_4 isomers in terms of energies, based on the results of a non-empirical calculation by the Hartree–Fock method[43], is illustrated in Fig.1. One should bear in mind that in this approximation the energies obtained for certain systems are much too high. This applies particularly to cyclobutadiene (IX) and one must therefore expect that the difference between the energies of tetrahedrane and cyclobutadiene is much greater than 30–50 kcal mole^{-1}. An adequate description of the above system becomes possible when configurations with open shells are introduced into the wave function. In the calculations taking into account the configuration interaction the energy of the ground state of tetrahedrane is found to be higher by 70.3 kcal mole^{-1} than that of cyclobutadiene[41]. Similar values (73–84 kcal mole^{-1}) are given by the semi-empirical PPP, PNDO, and MINDO methods[36,38,39]. Comparison of the energies of cyclobutadiene and two acetylene molecules leads to highly conflicting results, depending on the method of calculation. Thus, according to semi-empirical calculations, the energy of the cyclobutadiene molecule is lower than that of the pair of acetylene molecules by an amount ranging from 2 to 50 kcal mole^{-1}.[36,44] However, the results of a non-empirical calculation by the method of configuration interaction, according to which the pair of acetylene molecules has a lower energy than that of the cyclobutadiene molecule, are more reliable, the difference being estimated as 0–30 kcal mole^{-1}.[37,41] If one takes into account the lower limit of the semi-empirical estimate, then, presumably, cyclobutadiene and a pair of acetylene molecules constitute virtually isoenergetic systems.

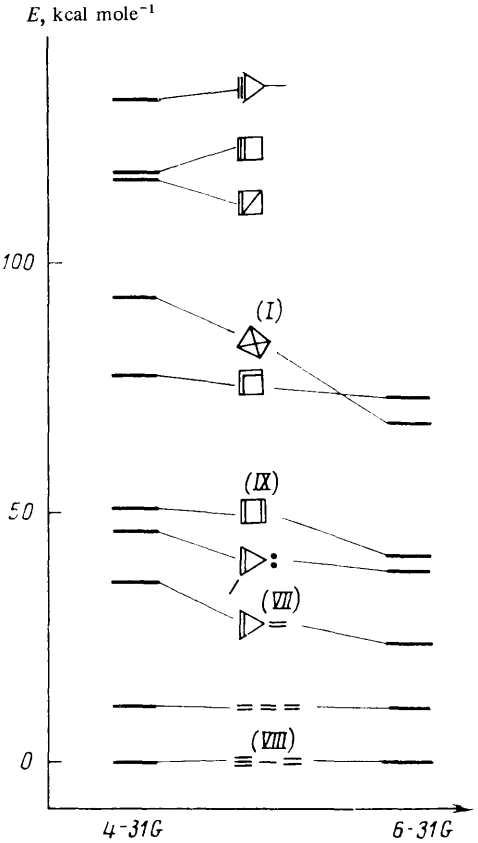


Figure 1. The relative energies of a number of C_4H_4 isomers (relative to but-3-en-1-yne) calculated in terms of the one-determinant approximation of the MO SCF method using 4-31 G and 6-31 G extended Gaussian basis sets[43].

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‡ The simple Hückel molecular orbital method leads to a triplet configuration for the ground state of cyclobutadiene. For further details, see Dewar and Gleicher[36] and Buenker and Peyerimhoff[37].

When the possible pathways towards the isomerisation of tetrahedrane are considered, direct conversion into cyclobutadiene or decomposition into two acetylene molecules are thought to be unlikely, since these processes are forbidden by the principle of the conservation of orbital symmetry[42]. The most probable initial stage in the isomerisation is the dissociation of one of the C–C bonds with formation of the bicyclobutyl biradical (X). According to the results of a non-empirical calculation, the planar biradical should have an energy higher by 30–50 kcal mole^{-1} than that of tetrahedrane and higher by 100–120 kcal mole^{-1} than that of cyclobutadiene[41]. Estimation of the energy of the non-planar biradical with the geometry of bicyclobutane itself by semi-empirical methods leads to higher values than the energy of tetrahedrane by an amount ranging from 2 to 11 kcal mole^{-1}.[39] The equilibrium geometry of the biradical was not determined, since the above estimates are only approximate. Nevertheless they permit the assumption that tetrahedrane and the bicyclobutyl biradical have similar energies, that of the biradical being lower. The most probable schematic distribution of energy levels corresponding to tetrahedrane, cyclobutadiene, the biradical (X), and a pair of acetylene molecules, constructed on the basis of the above calculations, is presented in Fig. 2.

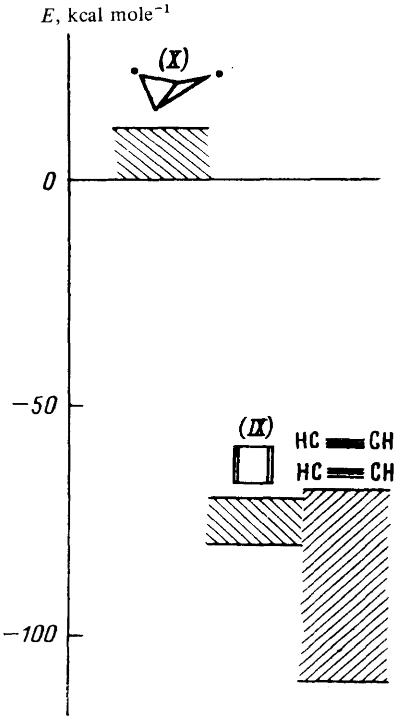


Figure 2. The probable energy ranges of the possible tetrahedrane conversion products (the tetrahedrane energy was adopted as the zero level).

The enthalpies of formation of tetrahedrane at 0 K, estimated from the total energies calculated by different methods, agree to within 15 kcal mole^{-1}; the following values have been obtained: 146.1 kcal mole^{-1} (PNDO method[38]), 135.2 kcal mole^{-1} (MINDO method[39,40]), and 129–137 kcal mole^{-1} (non-empirical calculation by the MO SCF method in terms of an extended Gaussian basis set[42]). The strain energy in tetrahedrane is estimated as 142.8 kcal mole^{-1} with a deviation from additivity (i.e. from the sum of the strain energies of the four three-membered rings) of 18.0 kcal mole^{-1}.[40] The first ionisation potential of tetrahedrane (the removal of an electron from the 1*e* orbital), calculated in terms of the PNDO approximation, is 9.58 eV,[38] in good agreement with the non-empirical calculation, which gives 10.35 eV.[41] For comparison, we may indicate the ionisation potentials of certain hydrocarbons[45]: 12.71 eV for methane, 11.50 eV for ethane, 11.07 eV for propane, 10.63 eV for n-butane, 10.6 eV for cyclobutane, 10.06 eV for cyclopropane, 9.45 eV for spiropentane, and 8.74 eV for cubane.

As already mentioned, the construction of the complete potential energy hypersurface for the C_4H_4 system is too difficult. However, in the region of the equilibrium geometry of tetrahedrane the calculation of the potential energy surface becomes possible in view of the high symmetry of the molecule. The number of types of normal vibrations is 8, and the potential energy matrix contains only 13 independent elements (without taking into account the symmetry, the number of the independent matrix elements would have been 171). Calculation performed by the non-empirical MO SCF method yields positive force constants for all the normal vibrations[42], which means that a local minimum on the C_4H_4 potential energy surface corresponds to tetrahedrane. The equilibrium geometrical parameters are $R_{\text{C-H}} = 1.054$ Å and $R_{\text{C-C}} = 1.482$ Å, the accuracy of the determination of which is estimated as to within 0.01 Å. The force constants for the extension of the C–H and C–C bonds proved to be 6.5 and 4.6 mdyn Å^{-1} respectively. Comparison with other hydrocarbons permits the conclusion that the C–H bond in tetrahedrane is similar to the analogous bond in acetylene, while the C–C bond is close to the ordinary single bond.

Sections through the potential energy surfaces of the excited electronic states of tetrahedrane, corresponding to the extension of the C–C bonds with a fixed C–H distance and retention of tetrahedral symmetry, have also been obtained[41]. It was found that none of the excited states is bound in relation to such deformation, at least for C–C distances ranging from 1.38 to 1.69 Å.

The possibility of the prolonged existence of an isolated tetrahedrane molecule can be inferred from the estimate of the barrier to the transformation into the bicyclobutyl biradical (X).[42] It has been suggested that motion along the reaction coordinate along the initial section corresponds to an increase in the length of one of the C–C bonds with a simultaneous change of the C–C–H angles. With increase of the distance between the nuclei of the C–C bond ruptured in this transformation to 1.812 Å (which corresponds to an increase in the dihedral angle between the three-membered rings of approximately 20°) and following the optimisation of the C–C–H angles, the energy increases by 18 kcal mole^{-1} compared with that of the equilibrium tetrahedral configuration. This value is adopted as the lower limit of the potential barrier. Calculation for the first excited triplet state of the deformed tetrahedrane molecule yields 45 kcal mole^{-1} as the vertical excitation energy, whence it follows that the excited state does not influence the initial stage of the isomerisation process.

2. The Electronic Structure of the Tetrahedrane Molecule

In order to elucidate the nature of the chemical bonds in the tetrahedrane molecule, it is of interest to calculate the distribution of electron density and to analyse the wave functions. The distribution of the valence electron density has been calculated[46] by the extended Hückel method. In each of the three-membered tetrahedrane rings, the electron density is distributed in the same way as in the cyclopropane molecule. In particular, there are two electron density maxima on the outer side of each of the edges of the tetrahedron formed by the straight lines joining the C nuclei. At the centre of the tetrahedron and in the centre of each face, the electron density has a minimum. Overall, the pattern obtained shows that the nature of the C–C bond in tetrahedrane is close to that of a single bond in saturated hydrocarbons and differs significantly from the acetylenic bond.

Much attention has been devoted to the study of the hybridisation in tetrahedrane[42,47–49]. According to the results of various calculations, the localised hybrid molecular orbitals corresponding to the C–C bonds have 79–83% of *p* character and deviate from the direction of the bond by 30–39°. The hybrid molecular orbitals of the C–H bonds have 45–62% of *p* character. For comparison, we may note that the fractions of *p* character in the molecular orbitals of the C–C and C–H bonds of cubane are 80 and 61% respectively and that the distortion of the hybrid molecular orbital in the direction of the C–C bond is by approximately 11°. In cyclopropane the molecular orbitals of the C–C bonds have 81% of *p* character. Thus the amount of *p* character in the hybrid molecular orbitals of the C–C bonds in tetrahedrane is greater than in other saturated systems with small rings, which confirms the intuititive idea that the tetrahedrane structure involves maximum strain.

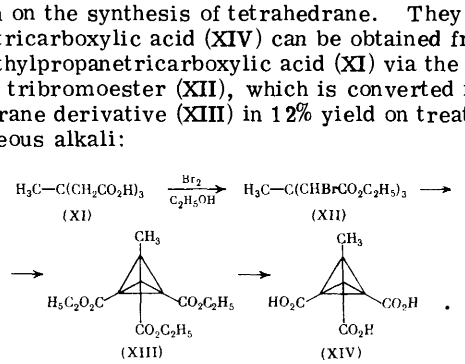
The correlation between the hybridisation parameters and the NMR constants has been used[42] to estimate the constants for the spin–spin interaction of the nuclei. The value $J_{^{13}\mathrm{C-H}}$ = 240 Hz obtained for tetrahedrane is intermediate between the values of $J_{^{13}\mathrm{C-H}}$ for cyclopropene (220 Hz) and acetylene (251 Hz). The value $J_{^{13}\mathrm{C-}^{13}\mathrm{C}}$ = 7.1 Hz for tetrahedrane is smaller than for cyclopropane (10 Hz) and bicyclobutane (21 Hz).

In conclusion, we may mention the theoretical prediction of the reactivity of tetrahedrane. The results of a study of the interaction of the valence electrons with an external charge within the framework of the electrostatic model based on the Hellmann–Feynman theorem have been used to examine the protonation reaction[50]. The equilibrium constant obtained shows that the tetrahedrane molecule should be protonated at pH $\leqslant$ 16.2. Despite its extremely approximate nature, this estimate indicates a high reactivity of tetrahedrane.

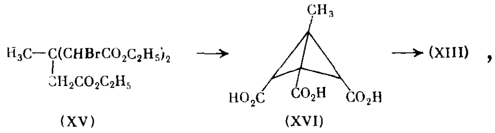
Summarising the theoretical studies, we may conclude that tetrahedrane corresponds to a metastable state of the C_4H_4 system and that the lifetime of an isolated molecule in the ground state may be fairly long. Electronic excitation should lead to the decomposition of the tetrahedrane molecule. Its high tendency towards protonation apparently necessitates the complete exclusion of all compounds containing mobile hydrogen atoms in attempts at synthesis.

III. EXPERIMENTAL APPROACHES TO THE SYNTHESIS OF TETRAHEDRANE

Beesly and Thorpe[51] were the first to propose a method for the synthesis of a compound having the tetrahedrane structure and must be regarded as the pioneers in the research on the synthesis of tetrahedrane. They found that the tricarboxylic acid (**XIV**) can be obtained from ββ-dimethylpropanetricarboxylic acid (**XI**) via the corresponding tribromoester (**XII**), which is converted into the tetrahedrane derivative (**XIII**) in 12% yield on treatment with aqueous alkali:

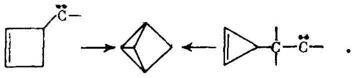


They also quote the experimental conditions for the synthesis of compound (**XIII**) from the tricarboxylic acid (**XIV**) formed on cyclisation of the dibromotriester (**XV**). The synthetic scheme and the absence of olefinic bonds according to the results obtained for the reaction of the product with bromine and potassium permanganate,



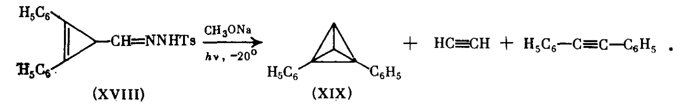
are believed to constitute proof of the proposed structure (**XIII**). In a separate article in the same volume of the Journal of the Chemical Society[52] Ingold carried out a simple calculation of the Baeyer strain and concluded that the existence of structures of this kind is possible.

For a long time chemists found the results of the above studies[51] surprising but reliable[53]. Furthermore, the ester formed by the acid (**XIV**) and cellulose was recommended for industrial manufacture[54] because of certain "useful" properties. However, almost forty years later Larson and Woodward[55] failed in their attempt to reproduce the synthesis of the acid (**XVI**) from compound (**XV**). When the latter was treated with an aqueous solution of alkali, the main reaction products were acetic acid and the initial acid (**XI**); no cyclic compounds could be isolated from the reaction mixture. The study by Larson and Woodward stimulated the development of research on the synthesis of highly strained compounds. The structure of tricyclo[1,1,1,$0^{2,5}$]pentane (**XVII**) was closest to that of tetrahedrane. It was obtained by two different methods in accordance with the following schemes[10,11,56]:

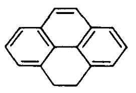


(XVII)

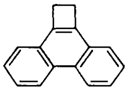
It is not fortuitous that compounds capable of generating in different ways a carbene centre linked to a cyclopropene ring have been proposed as precursors for the specific synthesis of tetrahedrane. Masamune and Kato[57] reported in 1965 the photochemical decomposition of the sodium salt of the tosylhydrazone of Δ^2-2,3-diphenylcyclopropenealdehyde (**XVIII**) into diphenyltetrahedrane with a yield of 0.1%. The structure of the product, having the overall formula $C_{16}H_{12}$ and a melting point of 133.5°C, was confirmed by infrared, ultraviolet, and ^{1}H NMR spectroscopic data. However a year later, the authors[58] proposed structures (**XX**) or (**XXI**) for the product of the above reaction, i.e. the structures of isomeric hydrocarbons which should have the same physicochemical characteristics as those proposed previously for the tetrahedrane derivative (XIX).



(XVIII) (XIX)

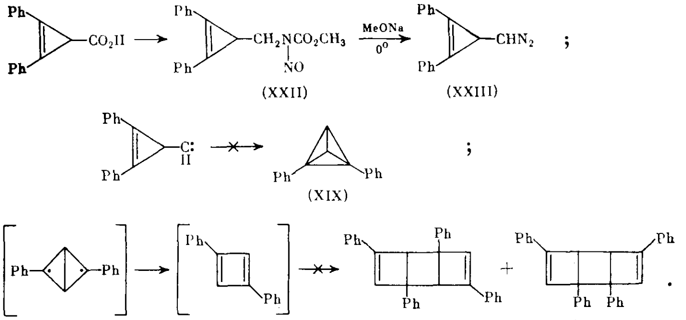


(XX)



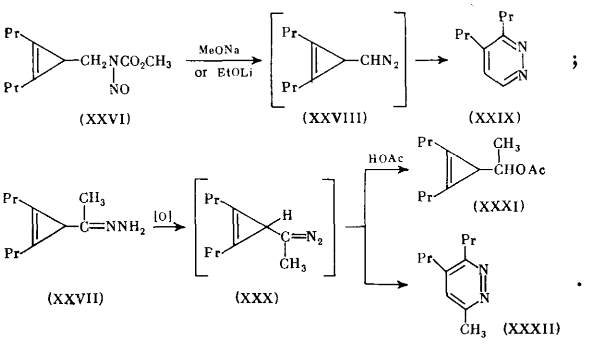
(XXI)

The prospect of using a substituted cyclopropenylcarbene attracted many investigators. For this reason, other reactions were used to generate this intermediate species and in all cases much attention was devoted to proving the formation of the carbene precursor—the corresponding diazo-compound. For example, Δ^2-2,3-diphenylcyclopropenyldiazomethane (XXIII), obtained[59] by treating with sodium methoxide the corresponding *N*-nitrosourethane (XXII), synthesised in six stages from 1,2-diphenylcyclopropenecarboxylic acid, was identified by its infrared spectrum. The diazoalkane (XXIII) proved to be extremely unstable in relation to the action of water and protic compounds. Its photolysis and thermolysis yielded neither tetrahedrane derivatives nor dimeric products based on cyclobutadiene.



(XXII) (XXIII) (XIX) (XXIV) (XXV)

The only product that could be identified was diphenylacetylene. The conditions for the synthesis and the reactivities of diazo-compounds of the cyclopropene series were carefully investigated somewhat later[60]. Two methods were used to synthesise them: the decomposition of the *N*-nitrosourethane (XXVI) and oxidation of the hydrazone (XXVII). The decomposition of the *N*-nitrosourethane by various bases and in different solvents led in all cases to a mixture of substances, among which only 3,4-dipropylpyridazine (XXIX) could be regarded as a product formed as a result of the 1,4-sigmatropic rearrangement of dipropylcyclopropenyldiazomethane (XXVIII).

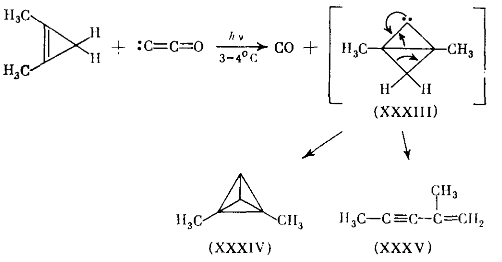


(XXVI) (XXVIII) (XXIX) (XXXI) (XXVII) (XXX) (XXXII)

Analysis of the reaction mixture obtained in the oxidation of the hydrazone (XXVII) by lead tetra-acetate or mercury(II) oxide also led to the conclusion that the corresponding diazo-compound is formed as an intermediate. Since the subsequent transformations of the diazo-alkane (XXX) into the corresponding pyridazine are slow, oxidation with lead tetra-acetate initially involves a faster decomposition of this unstable compound into the acetate (XXXI), while oxidation with mercury(II) acetate leads to the formation of the pyridazine (XXXII). The authors[60] do not quote data concerning the behaviour of the diazo-compounds on heating or irradiation but note that but-1-yne was not detected in any of the reactions.

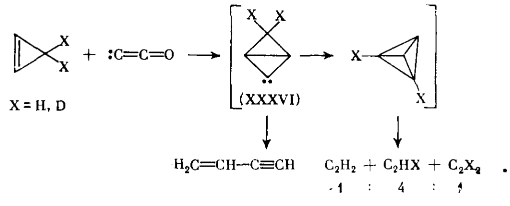
Another pathway, in which cyclopropene was also used as the initial compound, presupposed the intermolecular addition of the carbene generated from carbon suboxide. This method consisted in the photolysis of the latter in solution in 1,2-dimethylcyclopropene[61]. It was postulated that the carbene generated from C_3O_2 following the elimination of carbon monoxide may add to the olefinic bond of cyclopropene with formation of the intermediate bicyclic carbene (XXXIII), which may be stabilised by conversion into the tetrahedrane (XXXIV) as a result of intramolecular insertion into one of the C–H bonds.

$$C_3O_2 \xrightarrow{h\nu} CO + :C{=}C{=}O \ ;$$



(XXXIII) (XXXIV) (XXXV)

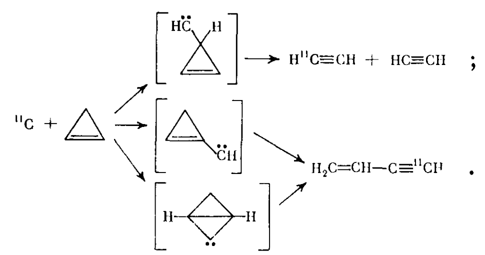
However, after irradiating the reaction mixture, it was possible to isolate only 2-methylpent-1-en-3-yne (XXXV) as the main photolysis product and pent-2-yne, which was formed as a result of the rearrangement of the initial 1,2-dimethylcyclopropene. The strain in the carbene (XXXIII) is apparently fairly high, so that its rearrangement to the acyclic hydrocarbon (XXXV) is faster than the intramolecular insertion with formation of the strained tetrahedrane ring. In a subsequent report Shelvin and Wolf[62] showed that, when a mixture of carbon suboxide and cyclopropene is irradiated, acetylene, which may be a product of the decomposition of the intermediate tetrahedrane, is formed in addition to vinylacetylene. The fact that acetylene is formed from tetrahedrane was confirmed using cyclopropene labelled with deuterium in the 3-position. Mass-spectrometric analysis of the acetylene fraction established that the compounds C_2H_2, C_2HD, and C_2D_2 are present in the reaction mixture in proportions of 1 : 4 : 1, which indicates the distribution of deuterium atoms at different carbon atoms of the tetrahedrane molecule, formed as a result of intramolecular insertion in the bicyclic carbene (XXXVI):



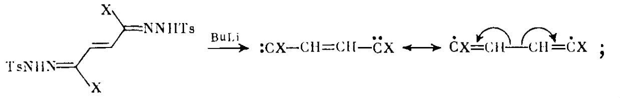
(XXXVI)

Additional data confirming the intermediate formation of tetrahedrane were obtained using carbon suboxide in which the central atom was labelled with ^{14}C. The authors[62] note that cyclobutadiene cannot be an intermediate in this reaction, because insertion of the ketocarbene in the C–D or the vinyl C–H bond should predominate in this case. However, it has been shown earlier that $:C_2O$ usually adds more readily to the multiple bond. Furthermore, the decomposition of cyclobutadiene into two acetylene molecules is also uncharacteristic[63].

Atomic carbon generated in a nuclear reactor and triplet carbonylcarbene generated by the photolysis of carbon suboxide have also been used as the carbene capable of adding to cyclopropene. Quantitative analysis of the composition of the reaction products led to the hypothesis of the intermediate formation of tetrahedrane in this case too:

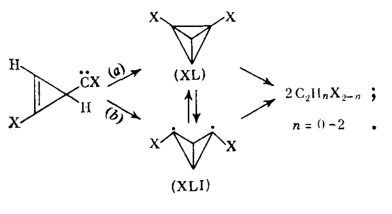


One of the possible approaches to the synthesis of tetrahedrane, which also included carbenes as intermediates, was proposed in 1973 by Rodewald and Lee[65]. They chose the bistosylhydrazone of *trans*-butenedial (XXXVII) as the source of the dicarbene. The decomposition products of the lithium salt of compound (XXXVII) at 140°C in tetrahydrofuran were collected at −80° and −190°C and investigated by preparative gas–liquid chromatography (GLC). Vinylacetylene, benzene, cyclo-octatetraene, and *syn*-$\Delta^{3,7}$-tricyclo[4,2,0,$0^{2,5}$]octadiene, which might have been formed from cyclobutadiene, were absent from the condensates. The only decomposition product was acetylene (unidentified polymers were also present). Having used the deuterium-labelled bistosylhydrazone (XXXVIII) as the starting material and having determined the distribution of the label by analysing the resulting acetylenes for deuterium, the authors proposed[65] the following mechanism for the formation of acetylenes with participation of tetrahedrane as one of the intermediates:



(XXXVII), X = H; (XXXVIII), X = D (1)

(2)

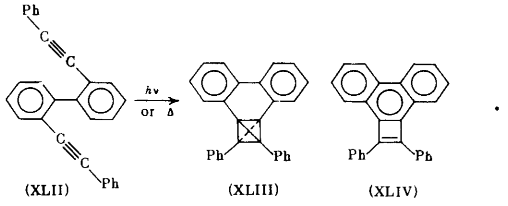


(3)

Only C_2HD may be formed in reactions (1) and (2). The proportions of C_2H_2, C_2HD, and C_2D_2 should be 1 : 4 : 1 for pathway (*a*) and 1 : 6 : 1 for pathway (*b*) (if the process is irreversible) or 1 : 4 : 1 [if the equilibrium between (XXXIX) and (XLI) is established 4–5 times faster than the rate of formation of acetylene]. The experimental distribution is 4.4% C_2D_2, 77.1% C_2HD, and 18.5% C_2H_2, showing that reaction (3) does occur and, although reactions (1) and (2) predominate, the tetrahedrane (XL) and the bicyclobutyl radical (XLI) serve as precursors of the acetylenes. Thus the determination of the quantitative composition of the acetylenes suggests that the intermediate (or the transition state) may be the symmetrical tetrahedrane or the biradical from which the tetrahedrane can also be formed.

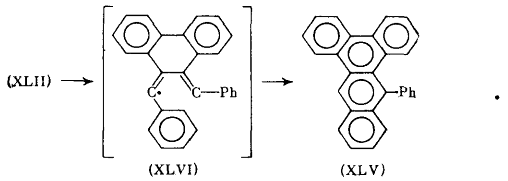
The dimerisation of acetylenes has been considered as another approach to the synthesis of tetrahedrane. In one of the first studies on these lines[66] it was shown that, when a mixture of acetylene and dideuteroacetylene is heated at 1200–1800 K, neither dimeric products nor HD are formed. The absence of deuterium exchange showed that tetrahedrane is not formed under these conditions.

However, Kandill and Dessy[67] reported in 1966 the possibility of the cyclisation of two acetylene groups into the tetrahedrane fragment. When 2,2′-di(phenylethynyl)-biphenyl (XLII) was photolysed or heated, an isomeric compound was obtained to which the structure of the tetrahedrane (XLIII) or the cyclobutadiene (XLIV) was attributed on the basis of the ultraviolet spectra:



(XLII) (XLIII) (XLIV)

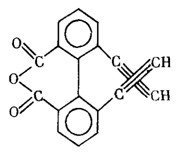
This structural assignment aroused a considerable controversy in the literature. White and Sieber[68] showed initially that the isomer obtained by Kandill and Dessy[67] is 9-phenyldibenzo[*a*,*c*]phenanthrene (XLV), which may be formed from the intermediate biradical (XLVI). Photolysis of compound (XLII) under different conditions and its subsequent thermolysis at 100°C did not lead to the formation of any compound other than (XLV):



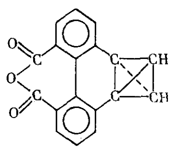
(XLVI) (XLV)

When compound (XLII) was heated at 150°C, compound (XLV) was again obtained together with unidentified compounds having high melting points and resembling phenanthrene according to their ultraviolet spectra. On the other hand, substances indicating at least the intermediate formation of tetrahedrane were not obtained in either thermal or photochemical processes.

Another diacetylene—6,6′-diethynyldiphenic anhydride (XLVII)—proved to be very stable under the conditions of pyrolysis (180°C) and photolysis[69]. No products, including those which might indicate the formation of the corresponding tetrahedrane (XLVIII), were found.

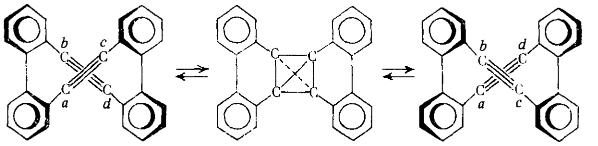


(XLVII)



(XLVIII)

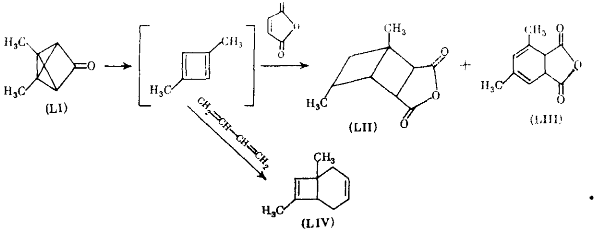
Nevertheless the idea of the possibility of synthesising tetrahedrane from acetylenes was not abandoned by investigators. For example, Staab and coworkers[70,71] undertook the synthesis of 9,10,19,20-tetradehydro[*a*,*c*,*g*,*i*]cyclododecene (XLIX)—a macrocyclic compound with crossed triple bonds in which structural factors favour the transannular interaction of the triple bonds. The possibility of such interaction was demonstrated by a number of chemical transformations, which justified the hypothesis that the acetylenic linkages are fairly close to one another. In order to confirm the possible formation of the tetrahedrane (L) from the diacetylene (XLIX), the authors[70,71] attempted to resolve the latter into enantiomers A and B and to detect the corresponding structural isomer which might have been formed by the irradiation of compound (XLIX) as a result of the transitions (XLIXA) ⇌ tetrahedrane ⇌ (XLIXB):



(XLIXA) (L) (XLIXB)

It was not possible to demonstrate the occurrence of photoracemisation, because the attempt to resolve compound (XLIX) into enantiomers chromatographically was unsuccessful. The authors[70,71] believe that the intermediate cyclobutadiene structure is preferable, but the problem whether it is formed from compound (XLIX) or via the tetrahedrane (L) remains open.

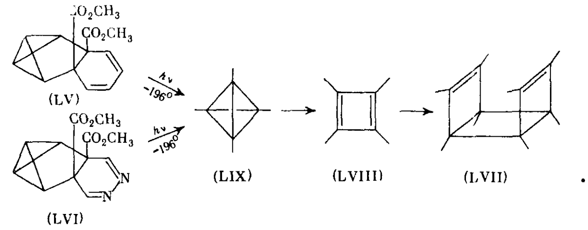
Yet another of the possible pathways to the synthesis of tetrahedrane was discovered by Masamune and coworkers[72], who investigated the thermolysis and photolysis of tricyclo[2,1,0,$0^{2,5}$]pentan-3-one. Thermolysis of the dimethyl derivative (LI) at 105.7° C gave very low yields of a mixture of compounds $C_{12}H_{16}$ (*m/e* 160), whose structures were not determined. Heating of compound (LI) in the presence of two equivalents of maleic anhydride was accompanied by the decomposition of the initial substance at a constant rate and led to the formation of compounds (LII) and (LIII). At a lower temperature (90°) only compound (LII) was detected; on heating, it rearranges to compound (LIII). When compound (LI) was treated with butadiene, a 30–40% yield of only 1,7-dimethylbicyclo[4,2,0]octa-3,7-diene (LIV) was obtained. On the basis of the composition of the products and the finding that the rate of decomposition of compound (LI) remains constant regardless of the presence of a "trapping agent", the authors[72] proposed a mechanism involving 1,3-dimethylcyclobutadiene as an intermediate and not the corresponding tetrahedrane:



(LI) (LII) (LIII) (LIV)

At the same time an attempt was made to investigate the composition of the photolysis products of compound (LI). It was irradiated with a high-pressure mercury lamp at 25° for 4 h until the attainment of 94% conversion of the initial compound. Acetylene (2%), propyne (6%), and butyne (2%) were found in the condensate collected at −190° C. By analogy with other studies, which were already discussed above, the authors[72] believe that the intermediate formation of tetrahedrane is probable in view of the presence of acetylene.

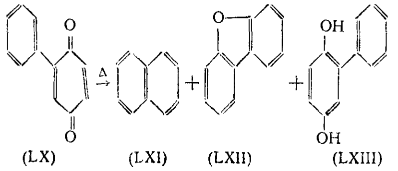
Polycyclic compounds (LV) and (LVI) have also been suggested as other tetrahedrane precursors containing the bicyclobutane fragment[73]. Photolysis of the diester (LV) in a matrix led to the formation of the cyclobutadiene dimer (LVII), but the authors[73] believe that the methyltetrahedrane (LIX) was formed as an intermediate and not tetramethylcyclobutadiene (LVIII), which could not be detected by infrared spectroscopy. It was suggested that the tetrahedrane isomerises to cyclobutadiene, which rapidly dimerises, the formation of the dimer (LVII) being faster than the valence [2 + 2] isomerisation (LIX) → (LVIII). As regards the transformation of the heterocyclic compound (LVI) owing to photolysis at 25° C, an analogous series of transformations [(LVI) → (LIX) → (LVIII) → (LVII)] was proposed on the basis of the composition of the products[73]:



(LV) (LVI) (LIX) (LVIII) (LVII)

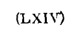
However, according to the literature[63], thermal isomerisation of tetrahedrane to cyclobutadiene is forbidden on symmetry grounds; the proposed mechanism is then incorrect.

Ions with the tetrahedrane structure have been detected in the mass spectra of certain compounds. For example, vacuum flash thermolysis (800° C) of phenyl-1,4-benzoquinone led to the isolation[74] of three substances: naphthalene (54%), 2-hydroxydibenzofuran (8%), and phenyl-1,4-hydroquinone (8%).

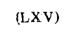


(LX) (LXI) (LXII) (LXIII)

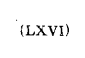
According to the authors[74], naphthalene is formed via a stage involving the loss of two CO molecules from phenyl-1,4-benzoquinone and subsequent intramolecular stabilisation of the butadiene biradical (LXIV), cyclobutadiene (LXV), or the tetrahedrane (LXVI). This hypothesis is based on the fact that the mass spectra of 1,4-benzoquinones[75] contain the peak of the $C_4R_4^+$ ion, which is more likely to represent a tetrahedrane than a substituted cyclobutadiene:



(LXIV)

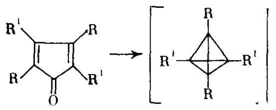


(LXV)



(LXVI)

The formation of the tetrahedrane structure (LXVII) has been observed[76] in the mass spectra also on fragmentation of substituted cyclopentadienols and cyclopentadienones:

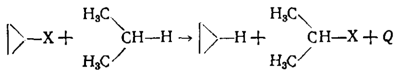


(LXVII)

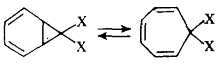
However, the determination of the exact structure of the ions in the gas phase by mass spectrometry is exceptionally difficult. A classical example is the controversy concerning the structure of the $C_7H_7^+$ ion to which the structure of the symmetrical propylium ion was attributed[77,78] on the basis of experiments with an isotope label, which was not confirmed by subsequent investigations[79,80]. Evidently the conclusion about the structure of ions of the type $C_4R_4^+$ and a reliable assignment of the tetrahedrane structure to the latter will become possible after a detailed investigation using the ion-cyclotron resonance technique[81].

---o0o---

Thus, despite the considerable efforts by both theoreticians and experimenters, the problem of tetrahedrane has not been solved. Furthermore, the main question whether or not tetrahedrane can exist as a stable (metastable) species remains obscure. Strictly speaking, the unsuccessful attempts at synthesis cannot be regarded as proof of the instability of the compound, and the history of organic chemistry confirms this[82]. Here one may note two approaches to the experimental solution of the problem. The first involves the fixation of tetrahedrane in a matrix and the demonstration (for example by spectroscopy) of its structure or its generation in the gas phase and direct (for example by electron diffraction) demonstration of its structure. In the second approach, tetrahedrane derivatives containing substituents capable of specific stabilisation of the tetrahedrane molecule are to be synthesised. The substituents can be selected on the basis of the following considerations, in the discussion of which valuable comments have been made by Prof. P. v. R. Schleyer. On the one hand, the stabilising effect of the substituents on the three-membered ring may be estimated by considering the heat of the following "isodesmic"[83,84] process:



Unfortunately the available literature, thermochemical data do not allow a broad comparison. On the other hand, data for certain "isodesmic" equilibria may serve as the starting point. As an example, one may quote the electrocyclic equilibrium of the norcarane (LXVIII) and cycloheptatriene (LXIX) structures. If the substituent X stabilises the three-membered ring specifically, then the equilibrium should be displaced to the left relative to X = H; if the substituent causes destabilisation, the shift should be to the right. Examination of the experimental data shows that the parent hydrocarbon (X = H) exists almost wholly in form (LXIX)[85,86], while the dicyano-derivative (X = CN) exists exclusively in form (LXVIII):



(LXVIII) (LXIX)

Thus the presence of cyano-groups should presumably stabilise the tetrahedrane skeleton (particularly bearing in mind the potential possibility of the ready protonation of tetrahedrane; see above). Furthermore tetracyanotetrahedrane would be of interest as a member of a class of nitrogen-carbon compounds (tetracyanomethane, tetracyanoethylene, and percyanoadamantane; for a systematic account of percyano-compounds, see Makhon'kov[87]), but consideration of this and related problems is outside the scope of the present review.

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Organic Peroxides of Alkali Metals (Alkali Salts of Hydroperoxides)

N.A.Sokolov and Yu.A.Aleksandrov

Methods of making non-solvated lithium, sodium, and potassium salts of hydroperoxides in hydrocarbon media are considered. Results on the kinetics and mechanism of thermal decomposition of alkali organic peroxides and the reactions of these compounds with alcohols, aldehydes, ketones, esters, and nitriles are discussed. The role of complex formation by the alkali salts of hydroperoxides with donors of protons and Lewis bases is considered. Methods of making organic and organoelemental peroxides based on salts of the hydroperoxides are discussed. 167 references.

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I. INTRODUCTION

Organic peroxides of Group I metals (salts of organic hydroperoxides) are peroxide compounds of the general formula ROOM, where R is an alkyl, aryl, or acyl radical, and M is a metal of Periodic Group I.[1] Organic peroxides (OP) of lithium, sodium, and potassium are now known. Analogous compounds of rubidium and caesium or of the metals of the copper subgroup have not been described.

Alkali metal OP's are of interest to investigators as starting materials for making the OP of elements of other groups[1-5], as intermediates in the autoxidation of organic derivatives of alkali metals, for the oxidation of hydrocarbons in the presence of alkalis, etc.

Ten years has elapsed since progress in the field of the chemistry of organic peroxides of the alkali metals was discussed[1]. This period has been marked by considerable range of investigations of metal-containing OP. Some of the results obtained for the OP are important in principle. All this has stimulated the preparation of the present review. It discusses, as far as possible, all the works on methods of synthesis and the investigation of the properties of the anhydrous OP, and also the kinetics and mechanism of conversion of salts of the hydroperoxides in aqueous or non-aqueous solutions. Works on the kinetics and mechanism of deformation decomposition of alkali salts of peroxo-acids and H_2O_2 are not included since this could be the subject of a special review.

II. METHODS OF PREPARATION

The simplest and most widely used method of making the alkali metal OP is based on the reaction of hydroperoxides with the metal hydroxide or alkoxide in aqueous or alcoholic solution respectively. This method is used widely for the separation and purification of hydroperoxides and in the preparation of dialkyl peroxides and esters of peroxo-acids. However, when hydroperoxides react with a hydroxide or alkoxide, usually crystalline solvates of hydroperoxide salts with water[6-9] or alcohol[10-12] are obtained. The water or alcohol cannot be removed completely from such solvates without decomposition of the initial peroxide.

Kharasch and coworkers[13] were the first to obtain sodium cumyl peroxide in hydrocarbon solution by reaction of the hydroperoxide with sodium or its amalgam. However, during this process 20–45% of the hydroperoxide, depending upon the nature of the solvent, was reduced to the alcohol and the alcohol and alkoxide formed are very difficult to separate from the sodium salt of the hydroperoxide. It seemed impossible to obtain the pure salt by this method[13,14]. A product containing 70–75% sodium cumyl peroxide was obtained by the reaction of cumyl hydroperoxide with metallic sodium in ether. The impurities were 1-methyl-1-phenylethanol (15–20%) and its alkoxide (10%).[14]

The alkali OP are formed as intermediates in the autoxidation of the corresponding organometallic compounds (OMC). However, the pure salt of the hydroperoxide usually also cannot be obtained by this method owing to its rapid reaction with the OMC [1]:

$$RM + O_2 \rightarrow ROOM \quad ,$$
$$RM + ROOM \rightarrow 2ROM \quad .$$

Peroxides were obtained in significant yield only in the oxidation of alkyl-lithium[15,16]. Thus the hydroperoxide was obtained in 28–67% yield in the autoxidation of butyllithium in ether or hydrocarbon solution at –75°C after hydrolysis of the lithium butyl peroxide formed[15,16]. 75–85% of the active oxygen was obtained in the autoxidation of indenyl-3-lithium in ether at –75°C.[16]

Non-solvated alkali metal OP were obtained by reaction of hydroperoxides with alkali metal amide, hydride, or t-butoxide at 0–20°C in an aprotic solution. Only slight reduction of the hydroperoxide took place. The gaseous products formed (ammonia, hydrogen) are easily removed; the solvent and t-butyl alcohol in the reaction with lithium t-butoxide) are also distilled off at reduced pressure[17].

The non-solvated salts were obtained from hydroperoxides by the action of lithium or sodium hydride in tetrahydrofuran or ether[18]:

$$ROOH + MH \rightarrow ROOM + H_2 \quad .$$

It was shown, by the examples of the reactions of tetralin hydroperoxide [1,2,3,4-tetrahydro-1-naphthyl hydroperoxide] with NaH in ether, and also of peracetic acid with LiH and NaH in tetrahydrofuran, that here (unlike the reaction of a hydroperoxide with a metal) it is not reduced[18]. However, it was recently noted[19] that when triphenylmethyl hydroperoxide reacts with NaH in ether the yield and purity of the sodium salt of the hydroperoxide are not very satisfactory.

Unlike peroxo-acids, the alkyl and arylalkyl hydroperoxides react very slowly with LiH at 20°C. Thus lithium hydride reacts rapidly, with evolution of heat, with perdecanoic acid[17], but for cumyl hydroperoxide the conversion is negligible even after 48 h.

The method most widely used for obtaining sodium and potassium OP is based on the reaction of a hydroperoxide with sodium[20-23] or potassium[24,25] amides in a hydrocarbon:

$$\mathrm{ROOH + MNH_2 \rightarrow ROOM + NH_3} \quad .$$

Pure sodium cumyl and triphenylmethyl peroxides were obtained for the first time by this reaction as were their solutions in a hydrocarbon free from significant amounts of impurities (alkoxide, alcohol, or hydroperoxide).[22,23] Hydroperoxides react rapidly with ground sodium or potassium amide at 0–20°C. Removal of ammonia from the reaction mixture by reducing the pressure facilitates an increase in the reaction rate[23-25]. It is noteworthy that an alkali metal amide should not contain as impurities ions of variable-valency metals, which decompose hydroperoxides readily. Therefore amides obtained by the reaction of a metal with liquid ammonia in the presence of an iron salt should not be used. Sufficiently pure sodium and potassium amides are easily obtained by passing ammonia through molten alkali metal at 350°C.[23,26]

When cumyl hydroperoxide reacts with sodium amide in toluene the sodium salt which is formed passes into the solution. After the almost complete removal of the toluene at reduced pressure and the addition of ether large crystals of sodium cumyl peroxide containing 99.5–99.8% of the main substance is obtained[22]. This compound readily absorbs moisture in the air but in a sealed vessel at 0°C remains without appreciable decomposition for several months[22].

Belyaev and Nemtsov[14] obtained a complex of sodium cumyl peroxide with cumyl hydroperoxide ROONa.ROOH. Cryoscopy showed that at a concentration of 0.08 M the complex is a dimer [ROONa.ROOH]$_2$ but dissociates to the monomer during dilution. In the infrared spectrum of the complex (in CCl_4), in addition to the narrow band of the vibrations of the OH group in the 3500 cm^{-1} range there is a broad band 350 cm^{-1} away in the lower frequency range. The displacement of the band of the OH vibrations is due to the formation of a hydrogen bond. The monomer of the complex is formed due to the hydrogen bond and the dimer is due to dipole–dipole interaction[14].

The thermodynamics of dissociation of the complex ROONa.ROOH (where R is cumyl) into the initial components was investigated by NMR.[27] The temperature dependence of the chemical shift of the proton of the OOH group was used to calculate the heat of dissociation of the complex, 12.7 ± 1.0 kcal mole^{-1}. The energy of the hydrogen bond in the complex is three times that in the hydroperoxide associate.

Potassium cumyl and t-butyl peroxides, sodium t-butyl peroxide, and also their complexes with hydroperoxide[24,25,28] have been obtained. Potassium t-butyl peroxide and its complex with the hydroperoxide were precipitated as they were formed in toluene or heptane. Under analogous conditions potassium cumyl peroxide appears in the solution. After removing the excess of potassium amide and distilling off the solvent at 20°C a viscous mass remains; when this is heated at 50°C and 0.1–0.5 mmHg a colourless solid containing 96–97% potassium cumyl peroxide is obtained. This compound deliquesces rapidly in air. In the absence of moisture at 0°C the active oxygen content had not decreased after 50 days. The salt thus obtained dissolved well in aromatic and aliphatic hydrocarbons and in ethers[25]. However crystalline potassium cumyl peroxide obtained by spontaneous crystallisation from toluene solution at 20°C does not dissolve in aprotic solvents[29].

When solutions of cumyl hydroperoxide and its potassium salt in heptane are mixed the complex

$$\mathrm{C_6H_5C(CH_3)_2OOK \cdot HOOC(CH_3)_2 \cdot C_6H_5}$$

is precipitated[25]. It seems that the hydrogen bond in the complex with the potassium salt should be stronger than those in the analogous sodium and lithium compounds, owing to the greater basicity of the K salt. The complexes of the hydroperoxide and its alkali salt are considerably less stable thermally than the non-solvated salts[14,22,25]. The decomposition temperature of potassium cumyl peroxide, determined thermographically, is 140–150°C, that is, 70–80 K higher than for its complex with cumyl hydroperoxide[25]. This is evidently due to weakening of the O–O bond in the complex under the influence of the hydrogen bond[30].

A method recently proposed for making salts of hydroperoxides was by the reaction of hydroperoxides with sodium bistrimethylsilylamide in ether[19]:

$$\begin{gathered}\mathrm{ROOH + NaN[Si(CH_3)_3]_2 \rightarrow ROONa + HN[Si(CH_3)_3]_2} \quad , \\ \mathrm{R = n\text{-}C_4H_9, \quad t\text{-}C_4H_9, \ (C_6H_5)_3C} \quad .\end{gathered}$$

This is a fast reaction. The sodium salt of the hydroperoxide was precipitated in high yield.

An attempt to obtain sodium triphenylsilyl peroxide $(C_6H_5)_3SiOONa$ by this method was unsuccessful. This compound decomposes in the presence of the strong base $NaN[Si(CH_3)_3]_2$, NaH, $NaNH_2$, or $n\text{-}C_4H_9Li$ even between −80° and −20°C with the formation of phenoxide and $[(C_6H_5)_2SiO]_x$.[19]

Lithium alkyl peroxides are obtained by the reaction of hydroperoxides with lithium t-butoxide in an aprotic solvent[17]:

$$\mathrm{ROOH + (CH_3)_3COLi \rightarrow ROOLi + (CH_3)_3COH.}$$

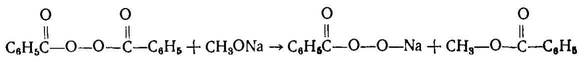
The reaction takes place readily at 0–20°C. Lithium t-butoxide has several advantages over alkoxides of primary and secondary alcohols and also over the analogous sodium and potassium compounds[17]. It is soluble in hydrocarbons therefore its solutions are readily obtained by heating the metal with a hydrocarbon solution of the alcohol[17,31,32]. t-Butyl alcohol and its alkoxides are stable in the presence of oxygen[32] or peroxides[33], whereas alcohols containing an α-hydrogen are oxidised readily by peroxides[33-36]. Alkoxides of primary and secondary alcohols are oxidised very readily by oxygen[32,37-39] and apparently by peroxides. Owing to steric hindrance and the acidic properties, t-butyl alcohol has less tendency to form complexes, especially with lithium salts, which have a lower basicity than the analogous sodium and potassium compounds. The lithium salts of the tertiary hydroperoxides are isolated after the solvent and t-butyl alcohol have been distilled off in a vacuum at 20°C. Thus lithium cumyl and lithium t-butyl hydroperoxides of 99.0–99.8% purity were first obtained in heptane[17]. Lithium cumyl peroxide is a white hygroscopic powder soluble in aromatic hydrocarbons. This peroxide ignites spontaneously when heated to 100–115°C. Lithium t-butyl peroxide is readily soluble in various organic solvents; when heated without a solvent it ignites spontaneously at 130–135°C.[17]

The lithium, sodium, and potassium salts of the primary hydroperoxides are insoluble in aprotic solvents and are immediately precipitated during the preparation[40,41]. The alkali salts of the secondary aliphatic hydroperoxides apparently also cannot be obtained in hydrocarbon or ethereal solution[41]. The poor solubility of the alkali salts of the primary and secondary hydroperoxides in aprotic solvents seems to be explained by the high degree of association of these salts. Even salts of tertiary hydroperoxides (namely, lithium and potassium cumyl peroxides) are associated into tetramers in benzene and cyclohexane[29].

Lithium salts of secondary arylalkyl hydroperoxides can be obtained in solutions. For example, solutions of lithium 1-phenylethyl peroxide in ether, heptane, and ethylbenzene have been obtained. However, after the solid salt had been isolated it did not redissolve in aprotic solvents. When 1-phenylethyl hydroperoxide reacts with lithium t-butoxide in ether, which is then removed at 0–20°C, a salt of the hydroperoxide (97% pure) is obtained, it ignites spontaneously at 91–92°C.[41]

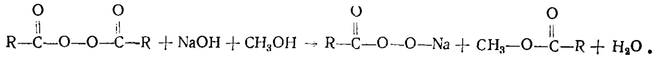
It is difficult to obtain the corresponding non-solvated salts by the reaction of hydroperoxides with potassium or sodium t-butoxide, since they rather firmly bond alcohol in a complex, unlike the analogous lithium compounds. The alcohol is difficult to remove from the complex ROOK.HOC$(CH_3)_3$ (where R is cumyl) even by heating in a vacuum[25]. True, potassium t-butyl hydroperoxide with a little t-butyl alcohol as impurity is obtained by heating the complex at 50°C in a high vacuum[42]. Apparently it is no less complicated to obtain a non-solvated salt by the reaction of a hydroperoxide with sodium methoxide[43]. Here in addition to the formation of a stable solvate with methanol, the alcohol and its alkoxide can be oxidised.

The sodium salts of acyl hydroperoxides (peroxo-acids) are made by reaction with sodium hydroxide. Anhydrous salts can be obtained with the aid of this reaction[44]. Sodium perbenzoate is usually made by the reaction of sodium methoxide with benzoyl peroxide in a mixture of alcohol and chloroform:



$$C_6H_5\overset{O}{\overset{\|}{C}}-O-O-\overset{O}{\overset{\|}{C}}-C_6H_5+CH_3ONa\rightarrow C_6H_5\overset{O}{\overset{\|}{C}}-O-O-Na+CH_3-O-\overset{O}{\overset{\|}{C}}-C_6H_5\ .$$

The same products are formed if instead of the alkoxide the alkali hydroxide in ethanol[45] or methanol[46] is taken:

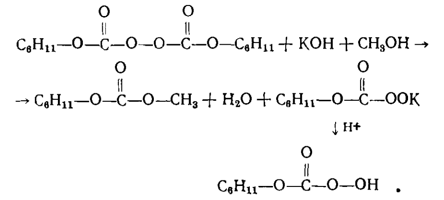


$$R-\overset{O}{\overset{\|}{C}}-O-O-\overset{O}{\overset{\|}{C}}-R+NaOH+CH_3OH\rightarrow R-\overset{O}{\overset{\|}{C}}-O-O-Na+CH_3-O-\overset{O}{\overset{\|}{C}}-R+H_2O\ .$$

The explanation[46] is that when the water concentration is low the equilibrium of the reaction

$$CH_3OH+{}^-OH\rightleftharpoons CH_3O^-+H_2O$$

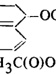
is shifted almost completely to the right[47]. The methoxide ion formed is more nucleophilic than the hydroxide ion[48]. *O*-cyclohexylmonoperoxocarbonic acid was obtained and isolated in the pure state by the reaction of dicyclohexylperoxodicarbonate with potassium hydroxide in methanol followed by the action of acid. It is evidently the first representative of an *O*-alkylmonopercarbonic acid[46].



$$C_6H_{11}-O-\overset{O}{\overset{\|}{C}}-O-O-\overset{O}{\overset{\|}{C}}-O-C_6H_{11}+KOH+CH_3OH\rightarrow$$
$$\rightarrow C_6H_{11}-O-\overset{O}{\overset{\|}{C}}-O-CH_3+H_2O+C_6H_{11}-O-\overset{O}{\overset{\|}{C}}-OOK$$
$$\downarrow H^+$$
$$C_6H_{11}-O-\overset{O}{\overset{\|}{C}}-O-OH\ .$$

Individual alkali metal OP and methods for making them are listed in Table 1.

Table 1. Methods of making organic peroxides of the alkali metals.

Peroxide	Method of preparation	Ref.
$(CH_3)_3COOLi$	ROOH + $(CH_3)_3COLi$ (heptane, 20°)	17
$C_6H_5C(CH_3)_2OOLi$	ROOH + $(CH_3)_3COLi$ (heptane, 20°)	17
$C_6H_5CH(CH_3)OOLi$	ROOH + $(CH_3)_3COLi$ (ethyl ether, 20°)	41
$CH_3C(O)OOLi$	ROOH + LiH (tetrahydrofuran)	18
$C_6H_5C(CH_3)_2OONa$	ROOH + $NaNH_2$ (toluene, 20°)	22
$(C_6H_5)_3COONa$	ROOH + $NaNH_2$ (toluene, 20°)	23
$(CH_3)_3COONa$	ROOH + $NaN[Si(CH_3)_3]_2$ (ether)	19
$CH_3CH_2CH_2CH_2OONa$	ROOH + $NaN[Si(CH_3)_3]_2$ (ether)	19
—OONa	ROOH + NaH (ether)	18
$CH_3C(O)OONa$	ROOH + NaH (ether)	18
$CH_3CH_2CH_2C(O)OONa$	ROOH + NaOH (water, alcohol, 0°)	44
$HC(O)OONa$	ROOH + NaOH (water, alcohol, 0°)	49
$C_6H_5C(CH_3)_2OONa.HOOC(CH_3)_2C_6H_5$	ROONa + ROOH (cumene, pentane)	14
$C_6H_5C(CH_3)_2OONa.HOOC(CH_3)_2C_6H_5$	ROONa + ROOH (toluene, heptane)	22
$(CH_3)_3COONa.HOOC(CH_3)_3$	2ROOH + C_2H_5ONa (toluene + ethanol, 20°)	28
$(CH_3)_3.COONa.(CH_3)_3COH$	ROOH + $(CH_3)_3CONa$ (t-butyl alcohol)	10
$C_6H_5(CH_3)_2COOK$	ROOH + KNH_2 (toluene, 20°)	25
$(CH_3)_3COOK$	ROOH + KNH_2 (toluene, 20°)	25
$(CH_3)_3COOK$	heating $(CH_3)_3COOK.(CH_3)_3COH$ in a high vacuum, 50°	42
$(C_6H_5C(CH_3)_2OOK.HOOC(CH_3)_2C_6H_5$	ROOH + KNH_2 (toluene, 20°)	25
$(CH_3)_3COOK.HOOC(CH_3)_3$	ROOH + KNH_2 (toluene, 20°)	25
$(CH_3)_3COOK.2HOOC(CH_3)_3$	ROOH + KNH_2 (toluene, 20°)	25
$(CH_3)_3COOK.(CH_3)_3COH$	ROOH + $(CH_3)_3CONa$ (t-butyl alcohol)	10
$(CH_3)_3COOK.C_2H_5OH$	ROOH + KOH (ethanol, 0–2°)	12

III. THERMAL DECOMPOSITION

Studies of the decomposition of the alkali metal OP can be divided into three groups, depending upon the subject and conditions of the investigation. The first group comprises investigations [13,22,29] in which the thermal decomposition of the non-solvated compounds in hydrocarbons was studied. The second group covers the investigation of the thermal decomposition of complexes of the alkali OP with water and hydroperoxide in hydrocarbon solutions. Most of the papers relate to the third group; they describe an investigation of the decomposition of hydroperoxides in aqueous-alkaline solutions. An alkali salt of the hydroperoxide is an intermediate product of this reaction.

The thermal decomposition of the alkali OP in hydrocarbons at 80–130°C has been investigated[29]. The decomposition of potassium cumyl peroxide is described by a first-order kinetic equation. The hydrocarbon used as solvent has little effect on the rate of decomposition of the peroxide (Table 2). The decomposition products are given in Table 3.

Table 2. Kinetic parameters of the thermal decomposition of the alkali organic peroxides (c_0 = 0.1 M).[29]

Peroxide	Solvent	10^5k, s^{-1} (at 110°C)	E, kcal $mole^{-1}$	lg A
$C_6H_5C(CH_3)_2OOK$	n-nonane	13.3	28.6	12.3
$C_6H_5C(CH_3)_2OOK$	cumene	7.0	29.0	12.4
$C_6H_5C(CH_3)_2OOK$	*m*-xylene	7.1	29.3	12.6
$C_6H_5C(CH_3)_2OOK$	t-butylbenzene	7.2	29.2	12.6
$(C_6H_5)_2CCH_3OOK$	t-butylbenzene	30.7	24.2	10.3
$(C_6H_5)_3COOK$	t-butylbenzene	18.4	21.4	8.5
$C_6H_5C(CH_3)_2OONa$	t-butylbenzene	19.7*	25.2	11.6

*10^4 k, litre $mole^{-1}$ s^{-1}.

A decomposition mechanism has been proposed[29]:

$$\begin{gathered}
\mathrm{ROO\,(L)}_n \rightarrow \mathrm{RO^{\bullet}} + {}^{\bullet}\mathrm{OK} + n\,\mathrm{L} \quad , \\
{}^{\bullet}\mathrm{OK} + \mathrm{SH} \rightarrow \mathrm{KOH} + \mathrm{S^{\bullet}} \quad , \\
\mathrm{RO^{\bullet}} + \mathrm{SH} \rightarrow \mathrm{ROH} + \mathrm{S^{\bullet}} \quad , \\
\mathrm{RO^{\bullet}} \rightarrow \mathrm{C_6H_5C\,(O)\,CH_3} + {}^{\bullet}\mathrm{CH_3} \quad , \\
\mathrm{C_6H_5C\,(O)\,CH_3} + 3\mathrm{ROOK} \rightarrow \mathrm{C_6H_5C\,(O)\,OK} + \mathrm{HC\,(O)\,OK} + 2\mathrm{ROH} + \mathrm{ROK} \quad , \\
\mathrm{S^{\bullet}} + \mathrm{S^{\bullet}} \rightarrow \mathrm{S{-}S} \quad .
\end{gathered}$$

During the decomposition of the associates there is a breaking of one peroxide bond after the act. The other peroxide molecules in the associate can be ligands (L) in relation to the decomposing molecule. A decrease in the strength of the peroxide bond being changed can be expected, as was noted for solvates with hydroperoxide and water[50]. The acetophenone formed in the partial decomposition of the cumyloxy-radicals readily undergoes a molecular reaction with potassium cumyl peroxide[51]. The yield of benzoic acid (a product of the oxidation of acetophenone) can be used to determine that the decomposition of the potassium salt of the hydroperoxide takes place by 60–80% by a free-radical reaction and 40–20% by a molecular reaction with the ketone. The ratio of the rates of these reactions depends on the nature of the solvent. The greater the rate of reaction of the free radical with the solvent, the less the part played by the molecular reaction.

Ethane is formed in the decomposition of potassium cumyl peroxide in n-nonane, but there are no gaseous products when the reaction is carried out in aromatic hydrocarbons. The explanation could be that the methyl radicals are added to the aromatic ring of the solvent[52] but are dimerised in nonane with formation of ethane[29]. The ${}^{\bullet}$OK radical evidently removes hydrogen from the solvent[53] with the formation of an alkali hydroxide. The absence of gaseous oxygen and of oxidation products of the solvent is characteristic[29]. The absence of oxygen in the decomposition of sodium cumyl peroxide in a hydrocarbon was noted earlier[13].

Table 3. Decomposition products of alkali organic peroxides (c_0 = 0.2 M).[29]

Peroxide	Reaction temp., °C	Solvent	Reaction time, h	Yield, moles per mole peroxide decomposed				
				$C_6H_5C(CH_3)_2OH$	$C_6H_5C(CH_3)_2OM$	$C_6H_5C(O)OM$	$HC(O)OM$	MOH
$C_6H_5C(CH_3)_2OOK$	110	n-nonane*	6	0.90	0.05	0.05	0.05	0.74
$C_6H_5C(CH_3)_2OOK$	110	cumene**	6	0.89	0.07	0.08	0.08	0.65
$C_6H_5C(CH_3)_2OOK$	110	t-butylbenzene	6	0.82	0.08	0.09	0.10	0.78
$C_6H_5C(CH_3)_2OONa$	120	t-butylbenzene	6	0.80	0.09	0.10	0.08	0.75
$C_6H_5C(CH_3)_2OOLi$	80	benzene	12	0.60	0.20	0.22	0.21	0.30
$C_6H_5C(CH_3)_2OOLi$	90	t-butylbenzene	6	0.83	0.09	0.11	0.11	0.74

*The decomposition products contain 0.03 mole ethane per mole peroxide decomposed.
**The bicumyl in the products was determined qualitatively.

Sodium and lithium cumyl peroxides decompose analogously. However, the kinetics of the processes differ significantly: the decomposition of the sodium salt is described by a kinetic equation for a second-order reaction, but the lithium salt decomposes with a clear induction period. Table 2 gives the kinetic parameters for the decomposition of sodium cumyl peroxide. The activation energy for the decomposition of lithium cumyl peroxide, calculated from the temperature dependence of the induction period, is 23.0 kcal $mole^{-1}$.[29]

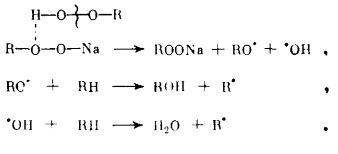
The difference in the formal kinetics of the decomposition of the peroxides is explained by the influence of the reaction products, above all the alkoxides. It seems that the formation of a complex of the peroxide with the alkoxide can change the strength of the O–O bond[29].

The decomposition of the salts in a hydrocarbon is greatly accelerated by additions of hydroperoxides, which is explained by the formation of the complexes ROOM.HOOR, which are less stable thermally[14,22,28,50]. The kinetics and mechanism of the decomposition of the complex

$$C_6H_5C(CH_3)_2OONa \cdot C_6H_5C(CH_3)_2OOH$$

in cumene have been studied[54,55]. The kinetic order with respect to the complex is 1.35, which the investigators explained by the occurrence of parallel reactions for the decomposition of the monomer and dimer of the complex (the latter is less stable thermally). The activation energy for the decomposition of the complex is 18.0 kcal $mole^{-1}$.[27,55] The decomposition of the complex initiates the polymerisation of styrene in bulk at 20–60°C more effectively than the decomposition of cumyl hydroperoxide. Belyaev and Nemtsov[55] think that the O-O bond of the hydroperoxide in the complex is broken, being weakened by the hydrogen bond. In the molecule of the salt, which is an acceptor of a proton, they think that the O-C and O-O bonds become stronger. However, other results[50] which will be considered below do not support these conclusions.

A mechanism for the decomposition of the complex is proposed:



$$\begin{array}{l} \text{H—O}\}\text{O—R} \\ \;\vdots \\ \text{R—O—O—Na} \longrightarrow \text{ROONa} + \text{RO}^{\bullet} + {}^{\bullet}\text{OH} , \end{array}$$

$$\text{RO}^{\bullet} + \text{RH} \longrightarrow \text{ROH} + \text{R}^{\bullet} ,$$

$$^{\bullet}\text{OH} + \text{RH} \longrightarrow \text{H}_2\text{O} + \text{R}^{\bullet} .$$

Acetophenone is formed as a result of the decompositon of the RO$^{\bullet}$ radical. Belyaev and Nemtsov[55] explain the yield of acetophenone being lower than in the thermal decomposition of the hydroperoxide by the increased strength of the C-CH_3 bond in the complexes. We think the small yield of acetophenone in the decomposition of these complexes is explained by ketones containing α-hydrogen being readily oxidised by salts of hydroperoxides and their complexes[51].

This scheme does not explain the formation of oxygen and 1-methyl-1-phenylethanol (1.5 moles per mole hydroperoxide decomposed). It is suggested therefore[55] that molecular decomposition of the dimer of the complex is more probable:

$$(\text{NaOOR})_2 \begin{bmatrix} \text{R—O—O—H} \\ \text{H—O—O—R} \end{bmatrix} \rightarrow 2\text{ROONa} + 2\text{ROH} + \text{O}_2 \quad .$$

The oxygen which has been formed by a chain free-radical mechanism oxidises cumene to its hydroperoxide, the decomposition of which also gives an additional amount of 1-methyl-1-phenylethanol.[55]

The decomposition of the complexes ROOK.ROOH and ROOK.$2H_2O$ (where R = cumyl) in benzene and toluene has been investigated[50]. The thermal decomposition of these complexes in solution is rather rapid even at 70-80°C. The main products of the reaction are 1-methyl-1-phenylethanol, potassium benzoate, and oxygen (Table 4). Potassium formate is also formed during decomposition in benzene[56].

Table 4. Decomposition products of the complexes with water and a hydroperoxide[50] (concentration 0.2 M).

Complex	Reaction temp., °C	Solvent	Yield, moles per mole complex decomposed		
			1-methyl-1-phenyl ethanol	potassium benzoate	oxygen
$C_6H_5C(CH_3)_2OOK \cdot 2H_2O$	80	toluene	1.0	0.29	none
$C_6H_5C(CH_3)_2OOK \cdot 2H_2O$	70	benzene	0.8	0.18	0.11
$C_6H_5C(CH_3)_2OOK \cdot C_6H_5C(CH_3)_2OOH$	70	toluene	2.0	0.38	0.24

The decomposition of the complex with water in benzene or toluene is described well by a first-order kinetic equation, as is the decomposition of the complex with the hydroperoxide in toluene. However the decomposition of this complex in benzene slows down sharply after the concentration of the peroxide compound has fallen to approximately half the initial value[50]. Table 5 gives the effective rate constants and activation energies for the decomposition of the complexes in benzene or toluene. The thermal decomposition of the complexes with loss of peroxide oxygen proceeds more readily than the decomposition of the potassium salt or the hydroperoxide separately.

Table 5. Rate constant and effective activation energies for the decomposition of the complexes of potassium cumyl peroxide with water and with a hydroperoxide (concentration 0.1 M).[50]

Complex	Solvent	$10^5 k$, s^{-1} at 70°C	E, kcal $mole^{-1}$
$C_6H_5C(CH_3)_2OOK \cdot 2H_2O$	benzene	19.4	25.3
$C_6H_5C(CH_3)_2OOK \cdot 2H_2O$	toluene	11.9	22.6
$C_6H_5C(CH_3)_2OOK \cdot C_6H_5C(CH_3)_2OOH$	toluene	40.8	19.3
$C_6H_5C(CH_3)_2OOK \cdot C_6H_5C(CH_3)_2OOH$	benzene	3.67*	23.9*

---

*$10^5 w_0$, mole $litre^{-1}$ s^{-1}.

**Calculated from the temperature coefficient of the initial rate.

Additions of an inhibitor (1-naphthylamine) do not affect the decomposition of the complex of potassium cumyl peroxide with water in toluene. This shows that a molecular reaction of the inhibitor with the peroxide compound does not occur, just like the chain reaction for decomposition.

The rate of loss of peroxide oxygen in the decomposition of the complex in cumene increases with the concentration of 1-naphthylamine. The explanation is that 1-naphthylamine inhibits the radical-chain oxidation of cumene to its hydroperoxide by the oxidation formed in the decomposition of the complexes. The rate of decomposition of 1-naphthylamine in benzene showed that 10-20% of the complex decomposes with formation of free radicals:

$$\text{ROOK} \cdot 2\text{H}_2\text{O} \rightarrow \text{RO}^{\cdot} + {}^{\cdot}\text{OK} + 2\text{H}_2\text{O} \quad ,$$

$$\text{ROOK} \cdot \text{ROOH} \rightarrow \text{RO}_2^{\cdot} + \text{RO}^{\cdot} + \text{KOH} \quad .$$

The complexes decompose predominantly by molecular reactions:

$$2\,[\text{ROOK} \cdot 2\text{H}_2\text{O}] \rightarrow 2\text{ROH} + 2\text{KOH} + 2\text{H}_2\text{O} + \text{O}_2 \quad ,$$

$$\text{ROOK} \cdot \text{HOOR} \rightarrow \text{ROK} + \text{ROH} + \text{O}_2 \quad ,$$

$$\text{ROK} + \text{ROOK} \cdot \text{HOOR} \rightarrow \text{ROH} + 2\text{ROOK} \quad .$$

The occurrence of the last exchange reaction is explained by the fact that decomposition of the complex of potassium cumyl peroxide with the hydroperoxide in benzene is greatly retarded after the concentration of peroxide oxygen has been reduced to approximately half.

The cumyloxy-radical detaches hydrogen from cumene and toluene to form 1-methyl-1-phenylethanol and a radical of the solvent, which is oxidised by the oxygen formed. In benzene, the cumyloxy-radical decomposes into the methyl radical and acetophenone, which is readily oxidised by potassium cumyl peroxide by a molecular mechanism[51]. In the decomposition of the complexes in toluene at 70° and 80°C, benzoic acid is formed due to oxidation of the solvent.

The lower thermal stability of the complex with water apparently shows the considerable drop in the dissociation energy of the O–O bond in the formation of a hydrogen bond. The influence of water cannot be explained by the formation of hydroperoxide due to the hydrolysis of its salt, since the degree of hydrolysis under the conditions of the reaction is low owing to the acidity of the hydroperoxide being much greater than that for water[50].

The decomposition of complexes of sodium t-butylperoxide with the hydroperoxide and water was investigated[28]. Sodium cumyl peroxide hexahydrate decomposes slowly at 60–70°C.[9] It loses active oxygen completely after 2 h at 115°C. Decomposition proceeds mainly according to the scheme:

$$C_6H_5C(CH_3)_2OONa \cdot 6H_2O \rightarrow C_6H_5C(CH_3)_2OH + \frac{1}{2}O_2 + NaOH + 5H_2O\ .$$

This main process is accompanied by the formation of acetophenone and methanol, which react with the initial compound:

$$\begin{gathered} C_6H_5COCH_3 + 4C_6H_5C(CH_3)_2OOH + 3NaOH \rightarrow \\ \rightarrow C_6H_5C(O)ONa + Na_2CO_3 + 3H_2O + 4C_6H_5C(CH_3)_2OH; \\ CH_3OH + 2C_6H_5C(CH_3)_2OOH + NaOH \rightarrow HCOONa + 2H_2O + 2C_6H_5C(CH_3)_2OH\ . \end{gathered}$$

The formation of a little bicumyl shows that free-radical decomposition of the hexahydrate takes place[9]:

$$C_6H_5C(CH_3)_2OONa \cdot 6H_2O \rightarrow C_6H_5C(CH_3)_2O^{\cdot} + {}^{\cdot}ONa + 6H_2O\ .$$

The radical which is formed removes hydrogen from the solvent. The solvent radicals are oxidised by the oxygen released in the molecular decomposition of the peroxide or are dimerised. Additions of the hydroperoxide accelerate the decomposition of sodium cumyl peroxide hexahydrate in cumene at 80°C.[8] The highest reaction rate was observed at a molar ratio of 2 : 1 between the hydroperoxide and its salt. Decomposition of the salt without addition of hydroperoxide was slower by a factor of almost 2. Kharasch and coworkers[13] obtained analogous results.

When mixtures of sodium cumyl peroxide hexahydrate with the hydroperoxide or 1-methyl-1-phenylethanol in cumene was heated briefly to 80°C and then cooled rapidly a crystalline trihydrate was precipitated. The formation of this compound is explained by the existence of the equilibrium[8]:

$$ROONa \cdot 6H_2O + n\,A \rightleftarrows ROONa \cdot 3H_2O + n\,A \cdot 3H_2O\ ,$$

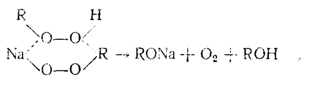
where A is an acceptor of water.

Kharasch and coworkers[13] proposed an ion-molecular mechanism for the decomposition of hydroperoxide:

$$RO_2^- + ROOH \rightarrow RO^- + ROH + O_2\ .$$

They think[13] that free radicals are not formed and postulate the direct transfer of the oxygen atom from the peroxide anion to a reductant, which could be the non-dissociated hydroperoxide molecule or an alcohol with an α-hydrogen atom.

A mechanism of alkaline decomposition of hydroperoxide into a six-membered cyclic active complex was proposed[3,57]:



Apparently, molecular decomposition of the complexes of alkali OP with hydroperoxide and water takes place in the six-membered cyclic active complex. However, as an analysis of the products shows[29] that such a mechanism does not take place in the decomposition of the non-solvated alkali OP on hydrocarbons. It seems that an important part in the molecular decomposition of salts of hydroperoxides with release of oxygen is played by their solvation with the formation of a hydrogen bond.

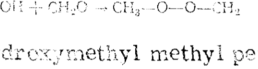
The decomposition of a hydroperoxide and its salt in water by a free-radical mechanism could be due to traces of metals of variable valency. This is shown by the decrease in the rate of formation of oxygen by additions of small quantities of EDTA.[58]

The kinetics of decomposition of cumyl hydroperoxide in the presence of NaOH in various solvents was studied recently[59]. The alkaline decomposition of *m*- and *p*-di-isopropylbenzene dihydroperoxides in aqueous solution and also the decomposition of the crystalline hydrates of their disodium salts were investigated[60,61]. The primary product of the alkaline decomposition of the dihydroperoxides are hydroxyhydroperoxides, and the final products are carbinols, acetylbenzenes, carbonic acids. Belen'kii and coworkers[61] suggest the formation of atomic oxygen, which oxidises the primary decomposition products. We think the formation of the acids is explained by the reaction of the dihydroperoxide salt with the ketone formed as intermediate product.

A method of alkaline decomposition of hydroperoxides on an ion-exchange resin containing an active group of a quaternary ammonium base has been proposed[62].

Primary and secondary hydroperoxides decompose in an alkaline medium much more rapidly than the tertiary compounds. However, the sodium salts of hydroperoxides which contain α-hydrogen can also be obtained and in certain instances isolated[63]. The main products from the alkaline decomposition of primary and secondary hydroperoxides are the corresponding aldehydes or ketones; alcohols and acids can also be formed. Hydrogen is produced in the alkaline decomposition of the lower primary alkyl hydroperoxides. A brief review of the reactions in the alkaline decomposition of primary alkyl hydroperoxides has been published[64].

Methyl hydroperoxide decomposes in alkaline solution to form hydrogen, methanol, and formic acid[65]. Ethyl hydroperoxide decomposes with release of a very small amount of gas but when formaldehyde is added hydrogen is released. It is formed as a result of the alkaline decomposition of an alkyl hydroxymethyl peroxide, which is an intermediate product:

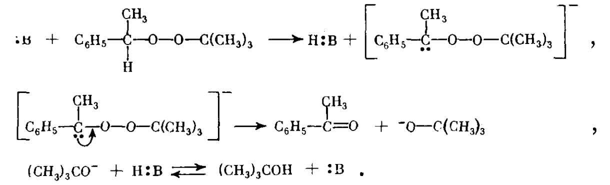


$$\begin{gathered} CH_3OOH \rightarrow CH_2O + H_2O \\ CH_3OOH + CH_2O \rightarrow CH_3{-}O{-}O{-}CH_2OH\ . \end{gathered}$$

Rieche[66] obtained hydroxymethyl methyl peroxide and ethyl hydroxymethyl peroxide. It was confirmed that these peroxides decompose in an alkaline medium with the formation of hydrogen, formic acid, and an alcohol, and in the second instance acetaldehyde also.

It was shown later[64] that n-butyl 1-hydroxyethyl and n-butyl 1-hydroxybutyl peroxides, unlike n-butyl hydroxymethyl peroxide, decompose in the presence of a base with the formation of a very small amount of gas. It was therefore concluded that hydrogen is formed from the hydroxymethylperoxo-group $O{-}O{-}CH_2OH$.

Not only hydroperoxides but also peroxides containing a hydrogen atom in the α-position decompose readily in an alkaline medium[67]. Peroxide compounds with either arylalkyl or alkyl radicals decompose readily. For example, 1,2,3,4-tetrahydro-1-naphthyl hydroperoxide is converted into α-tetralone [3,4-dihydro-1(2H)naphthalenone]. Isopropyl hydroperoxide rapidly forms acetone[68]. Kornblum and De La Mare[67] proposed a mechanism for the decomposition of peroxide compounds containing α-hydrogen, in the presence of a base (B):



$$:B + C_6H_5-C(CH_3)(H)-O-O-C(CH_3)_3 \longrightarrow H:B + [C_6H_5-\ddot{C}(CH_3)-O-O-C(CH_3)_3]^- ,$$

$$[C_6H_5-C(CH_3)-O-O-C(CH_3)_3]^- \longrightarrow C_6H_5-C(CH_3)=O + {}^-O-C(CH_3)_3 ,$$

$$(CH_3)_3CO^- + H:B \rightleftarrows (CH_3)_3COH + :B .$$

This mechanism is widely encountered (for example, cf. Hawkins[69]), but the formation of a carbanion in the decomposition of peroxide compounds, especially alkyl ones, in water or low-polar solvents, seems improbable.

Acrylonitrile does not retard the alkaline decomposition of tetralin hydroperoxide [1,2,3,4-tetrahydro-1-naphthyl hydroperoxide (Ed. of Translation)] in alcohol–water solution. The formation of a polymer during this reaction also is not observed, unlike the similar reaction in neutral solution. The explanation could be that free radicals are not formed in the alkaline decomposition of the hydroperoxide[70].

Syrkin and Moiseev[71] suggested that the alkaline decomposition of dialkyl peroxides containing an α-hydrogen proceeds in a cyclic transition state.

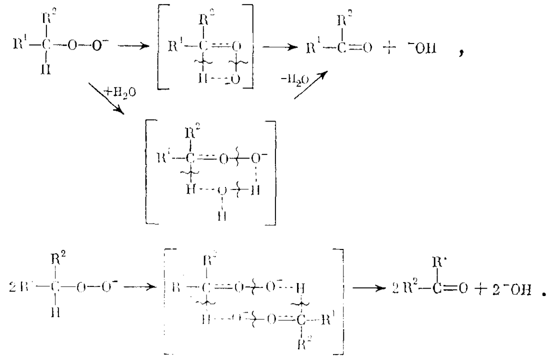
The kinetics of the alkaline decomposition of hydroperoxides with an α-hydrogen have been studied recently[40,41,72]. Hofmann and coworkers[72] investigated the kinetics of the decomposition of 4-n-heptyl, cyclohexyl, 1,2,3,4-tetrahydro-1-naphthyl, 1-phenylethyl, and cumyl hydroperoxides in methanol in the presence of sodium or potassium hydroxide. In addition to ketones, the decomposition products contained the corresponding alcohols. In investigating the kinetics of the process they obtained reproducible results only for 1,2,3,4-tetrahydro-1-naphthyl and 1-phenylethyl hydroperoxides. Additions of a little Complexone III did not alter the rate of decomposition of 1,2,3,4-tetrahydro-1-naphthyl hydroperoxide, but somewhat retarded the decomposition of 1-phenylethyl hydroperoxide and depressed the decomposition of the other hydroperoxides investigated (at 40°C). The inhibiting influence of the complexone is explained by these hydroperoxides decomposing according to a radical mechanism under the action of traces of heavy metal ions. The formation of alcohols is explained by the occurrence of free-radical reactions. The proportion of alcohols in the decomposition of the 1,2,3,4-tetrahydro-1-naphthyl and 1-phenylethyl hydroperoxides is insignificant. It is concluded that alkaline decomposition of these hydroperoxides proceeds according to the Kornblum–De La Mare mechanism.

The kinetics of decomposition of alkali salts of s-butyl and 1-phenylethyl hydroperoxides[41] and also of a substituted benzyl hydroperoxide[40] in aqueous solutions have been investigated. The rate constant of the first-order decomposition of a peroxide increases linearly with its initial concentration. The explanation could be that the decomposition proceeds by first- and second-order reactions in parallel:

$$w_{\text{eff}} = k_1c + k_2c^2;\ k_{\text{eff}} = k_1 + k_2c .$$

The straight lines obtained in coordinates of k_{eff} against c_0 were used to calculate the rate constants of the first- and second-order reactions at various temperatures. The rate of decomposition of the hydroperoxide salt in water is independent of the nature of the alkali cation (lithium, sodium, potassium)[40,41]. For the decomposition of the salt of s-butylhydroperoxide, $k_1 = 4.1 \times 10^8 \times \exp(-21\,000/RT)\ s^{-1}$, $k_2 = 3.2 \times 10^{11} \times \exp(-24\,700/RT)$ litre mole^{-1} s^{-1}; for the decomposition of the salts of 1-phenylethyl hydroperoxide $k_1 = 5.0 \times 10^6 \times \exp(-16\,500/RT)\ s^{-1}$, $k_2 = 6.7 \times 10^{11} \times \exp(-23\,000/RT)$ litre mole^{-1} s^{-1}.[41] The replacement of the ethyl group of the secondary hydroperoxide by a phenyl group considerably accelerates the decomposition of its alkali salt. The rate of decomposition of the sodium salts of the isomeric butyl hydroperoxides at 90°C fall in the order: primary > secondary > tertiary[41].

The simple composition of the products (during the decomposition of a salt of 1-phenylethyl hydroperoxide, acetophenone and the alkali hydroperoxide are formed quantitatively) and the low activation energy shows that decomposition of the peroxide anion with α-hydrogen takes place in a cyclic transition state. A six-membered transition state is the most favourable energetically, therefore the formation of such a state involving water is probable. Formation of an eight-membered cyclic transition state is suggested for a second-order reaction:



IV. REACTIONS WITH ORGANIC COMPOUNDS

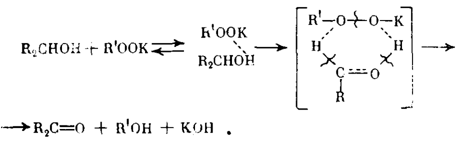
The alkali OP readily undergo nucleophilic substitution, addition, and elimination. The peroxide anion is a nucleophile with increased reactivity owing to the so-called α-effect.

The reactions of these peroxides with alkyl halides and acyl halides are nucleophilic substitutions and proceed with retention of the O–O bond and formation of dialkyl peroxides and peroxoacid esters respectively. Analogous reactions with organoelemental halogeno-derivatives are the main method for obtaining the OP of various elements. The primary stages of the reaction of hydroperoxide salts with carbonyl compounds and their heteroanalogues are nucleophilic additions. The decomposition of the salts of primary and secondary hydroperoxides with the formation of aldehydes and ketones are nucleophilic eliminations, as was discussed above[41,67,72].

The reactivity of the non-solvated alkali peroxides has been studied only recently[51,73-77]. Previously[78-86] the reaction of aqueous alkali salts of hydroperoxides with hydrocarbons[79,80], alcohols[13], aldehydes[81], ketones[81-84], and nitriles[13,58,78,86] were investigated. The reaction of the complex ROONa.ROOH with acetophenone and benzoquinone is also reported to take place comparatively readily[54,55]. It was found that even the addition of small quantities of water to a non-solvated peroxide greatly reduces its reaction rate with organic compounds[51] and can also change the composition of the products formed[75].

As already stated, the thermal decomposition of the non-solvated alkali OP in hydrocarbon solutions takes place at a significant rate only at 80–130°C.[29] However, in hydrocarbons in the presence of aldehydes, ketones, alcohols (with α-hydrogen), and esters these peroxides decompose rapidly even at 10–50°C.[51,73,76,77]. The rate of decomposition of the peroxide in the presence of these compounds increases in the order RQOLi < ROONa < ROOK. These reactions take place through intermediate complexes (with an alcohol) or peroxide compounds. Therefore when there is an excess of an organic compound the decomposition of the peroxide is described by a first-order kinetic equation and has zero or even negative order with respect to the other component[51,73,76].

As the initial concentration of diphenylmethanol is increased there is first an increase in the rate constant of the decomposition of potassium cumyl peroxide, which passes through a maximum at the equimolar ratio of the reagents, then decreases. This type of relation shows the formation of a 1 : 1 complex of the peroxide with the alcohol, a complex which decomposes readily with loss of the peroxide oxygen. The complex can be formed because of a hydrogen bond. The decomposition mechanism proposed for such complexes is through a six-membered cyclic transition state[73]:



The calculated kinetic parameters for the decomposition of the complexes of potassium cumyl peroxide with diphenylmethanol and 1-phenylethanol in benzene. For the complex with diphenylmethanol $k = 2.0 \times 10^9 \times \exp(-18\,300/RT)\ s^{-1}$, and for the complex with 1-phenylethanol $k = 2.5 \times 10^9 \times \exp(-18\,500\ RT)\ s^{-1}$.

Table 6. Kinetic parameters for the decomposition of lithium cumyl peroxide (0.1 M) in the presence of XC_6H_4CHO (0.4 M) in benzene.[76]

Substituent X	10^5k, s^{-1} (at 30°C)	E, kcal mole^{-1}	lg A
H	17.0	22.8	12.7
p-Cl	13.8	22.0	12.0
p-Br	15.8	22.8	12.7
p-CH_3O	29.2	18.3	9.7

The kinetics and mechanism of the reaction of lithium cumyl peroxide with benzaldehyde and substituted benzaldehydes at 20–40°C have been investigated in detail[76]. As the initial concentration of aldehyde is raised the rate constant for the decomposition of the peroxide first increases linearly, and then the increase slackens and stops. The analogous relation was obtained for the reaction of potassium cumyl peroxide with acetophenone, acetone, and ethyl methyl ketone.[51] This type of dependence of the rate of decomposition of the peroxide upon the concentration of the carbonyl compound is explained by the formation of an intermediate peroxide owing to the reversible nucleophilic addition of the peroxo-group to the carbonyl carbon. The decomposition of the intermediate peroxides proceeds through a cyclic transition state[76]:

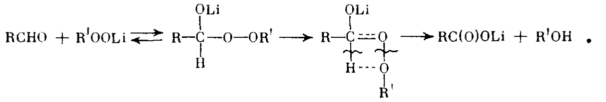
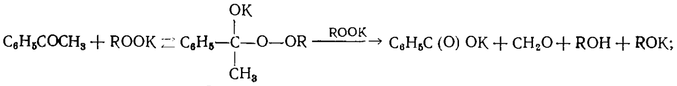


Table 6 gives the kinetic parameters of the decomposition of lithium cumyl peroxide in benzene in the presence of benzaldehyde or substituted benzaldehydes. The measurements were made in an excess of the aldehyde, when the equilibrium is shifted almost completely to the side of formation of an intermediate peroxide compound.

The reaction of potassium cumyl peroxide with acetophenone can be represented as[51]:



$$C_6H_5COCH_3 + ROOK \rightleftarrows C_6H_5-\underset{\displaystyle CH_3}{\overset{\displaystyle OK}{C}}-O-OR \xrightarrow{ROOK} C_6H_5C(O)OK + CH_2O + ROH + ROK;$$

$$CH_2O + ROOK \rightarrow HC(O)OK + ROH\ .$$

Table 7. Kinetic parameters for the decomposition of potassium cumyl peroxide (0.1 M) in the presence of ketones (0.4 M) in benzene.

Ketone	10^4k, s^{-1} (at 20°C)	E, kcal mole^{-1}	lg A
Acetophenone	5.5	16.4	9.0
Ethyl methyl ketone	2.8	14.7	7 4
Acetone	4.7	15.5	8.2

Table 7 gives the kinetic parameters for the decomposition of potassium cumyl peroxide in the presence of ketones. The results were obtained in an excess of the ketone, when a further increase in its concentration has little effect on the rate of decomposition of the peroxide. The kinetic parameters for Tables 6 and 7 relate to the slowest stage—the decomposition of the intermediate peroxide.

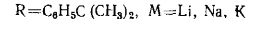
The alkali OP react with esters according to the scheme[77]

$$CH_3C(O)OC_2H_5 + 2ROOK \rightarrow 2CH_3C(O)OK + 2ROH \ (\text{at } 20°),$$

$$C_6H_5C(O)OC_2H_5 + 2ROOK \rightarrow C_6H_5C(O)OK + CH_3C(O)OK + 2ROH \ (\text{at } 70°).$$

The first stage of the reaction is evidently also nucleophilic addition of a peroxo-group to the carbonyl carbon. In this instance this stage is the slowest. Therefore the reaction is first order with respect to each reagent and second order overall.

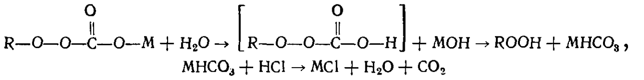
Carbon dioxide readily releases a hydroperoxide from its alkali salt in aqueous solution. This reaction is used widely for the separation and purification of the hydroperoxides. In the absence of water salts of the hydroperoxides in benzene are added to carbon dioxide with the formation of the alkali salts of arylalkyl monopercarbonic acids[74,75]:



$$R-O-O-M + CO_2 \rightarrow R-O-O-\overset{\displaystyle O}{\overset{\|}{C}}-O-M\ .$$

$R{=}C_6H_5C(CH_3)_2$, M=Li, Na, K

These compounds are hydrolysed by water with the formation of a hydroperoxide and when acidified carbon dioxide is also released. It seems that initially an unstable arylalkylmonopercarbonic acid is formed, which is decomposed into a hydroperoxide and carbon dioxide[74,75]:



$$\mathrm{R{-}O{-}O{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}O{-}}M + \mathrm{H_2O} \rightarrow \left[\mathrm{R{-}O{-}O{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}O{-}H}\right] + M\mathrm{OH} \rightarrow \mathrm{ROOH} + M\mathrm{HCO_3},$$
$$\mathrm{MHCO_3 + HCl \rightarrow MCl + H_2O + CO_2}$$

The reactions of hydrocarbons, aldehydes, and ketones with t-butyl and cumyl hydroperoxides in the presence of potassium hydroxide have been investigated[79-84]. An intermediate product is undoubtedly a hydrated salt of the hydroperoxide which is formed rapidly. Hydrocarbons (benzene, cumene, *p*-xylene, ethylbenzene, t-butyltoluene, tetralin, and *p*-isopropyltoluene) reduce hydroperoxides to alcohols at 70–80°C; oxygen is released only on heating in benzene. The alkyl groups of aromatic hydrocarbons are oxidised to alcohols, aldehydes, ketones, or carboxyl groups[79,80]. Thus *p*-xylene is mainly converted into *p*-methylbenzaldehyde and the corresponding acid, *p*-t-*p*-t-butyltoluene is oxidised to *p*-t-butylbenzyl alcohol, *p*-t-butylbenzaldehyde, and *p*-t-butylbenzoic acid, and ethylbenzene to acetophenone and benzoic acid. Goto and coworkers[79] suggested that the potassium salt of the hydroperoxide gives a complex with the hydrocarbon which is rearranged with the formation of oxidation products. However, it was shown later[50] that the decomposition of potassium cumyl peroxide hydrate in a hydrocarbon partly takes place with the formation of free radicals, which initiate the radical-chain oxidation of the hydrocarbons by the oxygen released.

Formaldehyde, acetaldehyde, and propionaldehyde are oxidised by hydroperoxide in aqueous alkaline solution at 25–35°C to the corresponding acids[81]. The reaction takes place through an intermediate peroxide which is formed in the reversible addition of the peroxide anion to the carbonyl carbon and decomposes by an ionic mechanism[81].

The reaction of t-butyl hydroperoxide with ketones in the presence of potassium hydroxide in chlorobenzene at 80°C has been investigated[82-84]. Diaryl ketones (benzophenone, *p*-nitrobenzophenone, and fluorenone)[82] do not change under these conditions. The main oxidation products of the arylalkyl ketones are the corresponding benzoic acid and an alcohol, obtained from the alkyl group of the ketone[83]:

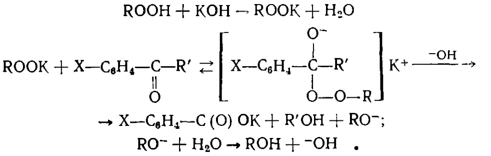
$$\mathrm{Ar{-}C\,(O){-}R \xrightarrow[KOH]{(CH_3)_3\,COOH} ArC\,(O)\,OH + ROH} \quad .$$

Thus in the oxidation of acetophenone and *p*-methylacetophenone the main products are methanol and the corresponding benzoic or *p*-toluic acid.

Aliphatic ketones react in two ways:

$$\mathrm{RC\,(O)\,R'} \xrightarrow[\mathrm{KOH}]{\mathrm{(CH_3)_3\,COOH}} \begin{cases} \rightarrow \mathrm{RC\,(O)\,OH + R'OH} \\ \rightarrow \mathrm{R'C\,(O)\,OH + ROH} \end{cases} \quad .$$

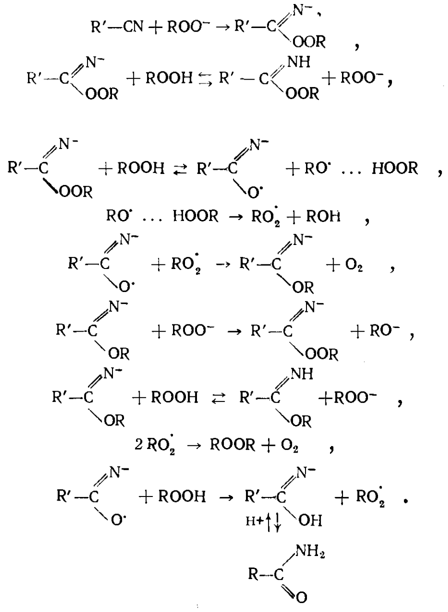
Maruyama[83,84] proposed the reaction mechanism:



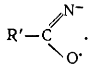
$$\mathrm{ROOH + KOH \rightarrow ROOK + H_2O}$$
$$\mathrm{ROOK + X{-}C_6H_4{-}\underset{\underset{\displaystyle O}{\|}}{C}{-}R'} \rightleftarrows \left[\mathrm{X{-}C_6H_4{-}\overset{\overset{\displaystyle O^-}{|}}{\underset{\underset{\displaystyle O{-}O{-}R}{|}}{C}}{-}R'}\right]\mathrm{K^+} \xrightarrow{^-\mathrm{OH}}$$
$$\mathrm{\rightarrow X{-}C_6H_4{-}C\,(O)\,OK + R'OH + RO^-;}$$
$$\mathrm{RO^- + H_2O \rightarrow ROH + {}^-OH} \quad .$$

The results of these investigations differ considerably from those obtained earlier[51]. In the oxidation of acetophenone by the aqueous potassium salt of a hydroperoxide in benzene at 70°C, benzoic and formic acids were observed[51]. Not one mole, but about three moles of the peroxide are decomposed per mole ketone oxidised.

Karasch and coworkers[13] found that the decomposition of cumyl hydroperoxide in the presence of 3 mole % of its sodium salt is strongly accelerated by an addition of 3–4% dinitriles, for example, succinonitrile. During this the hydroperoxide decomposes rapidly even at room temperature with the formation of 1-methyl-1-phenylethanol and oxygen. In this system secondary alcohols are oxidised rapidly to ketones. These investigators[13] suggested that nitriles form complexes with the hydroperoxide, which are readily decomposed without the formation of free radicals. A radical-chain mechanism was found later for the reaction[58,85,86]. Berger[86] proposed a scheme for the decomposition of t-alkyl hydroperoxides in the presence of a substituted benzonitrile and a base:



The first stage of the reaction is the addition of a peroxide anion to the nitrile group with the formation of an intermediate peroxide. This peroxide decomposes at the O–O bond with formation of an alkoxy-radical and a stable anion-radical



The radicals react with the hydroperoxide to give a peroxy-radical. The reactions of the latter lead to the formation of oxygen. According to the scheme one molecule of the nitrile decomposes several molecules of the hydroperoxide; the nitrile is gradually converted into an amide.

The peroxide anion, which contains in its composition a nitrile group, is unstable. Thus the hydroperoxide

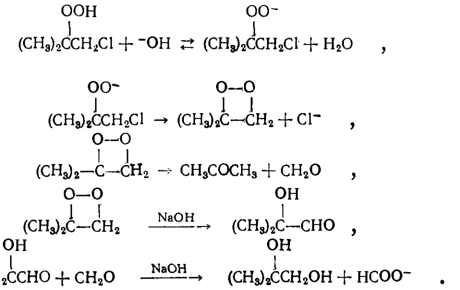
$$\mathrm{(CH_3)_2C(CN)OOH,}$$

unlike other tertiary hydroperoxides, decomposes readily in the presence of alkali. The decomposition products are acetone and cyanate ion[87].

To investigate the factors which determine the size of the α-effect in nucleophiles, the reactivity of the peroxide anions in substitutions at the saturated and aromatic carbon atom and also in reactions with carbonyl and nitrile carbon atoms in aqueous solution was studied[78].

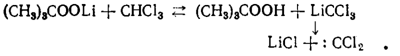
The kinetics of the reactions between organic halogen derivatives (*o*-chlorobenzyl chloride, allyl bromide, propyl bromide) and potassium t-butyl peroxide at 30° and 50°C in methanol have been investigated[88]. The activation energy is 21–23 kcal $mole^{-1}$. The activation energies for the reactions of organic halogeno-derivatives with alkoxides are similar.

The intramolecular reaction of the peroxide anion with the halogen derivatives takes place during decomposition of chloro-t-butyl hydroperoxide with an aqueous methanol solution of NaOH at 16–40°C.[89]



The decomposition of the intermediate 1,2-epidioxyethane is the limiting stage. At initially equimolar concentrations of hydroperoxide and alkali, 1,2-epidioxyethane decomposes with the formation of acetone and formaldehyde. When there is an excess of NaOH the rate of conversion of 1,2-epidioxyethane into the hydroxyaldehyde becomes considerable.

Petukhov and coworkers[90] studied the interaction of lithium t-butyl peroxide with polyhalogenomethanes. As in the reaction of polyhalogenomethanes with lithium alkyls the intermediate product is a halogenomethyl derivative of lithium, which decomposes with the formation of a halogenocarbene:



$$\begin{array}{l}(CH_3)_3COOLi + CHCl_3 \rightleftarrows (CH_3)_3COOH + \underset{\displaystyle LiCl + :CCl_2}{\underset{\downarrow}{LiCCl_3}}\end{array} \quad .$$

The formation of halogenocarbenes is proved by the production of a halogenonorcarane in the presence of cyclohexene.

V. USE

Preparation of Organic and Organometallic Peroxides

The method used most frequently is based on the reaction of nucleophilic replacement of a halogen atom in the corresponding organic or organometallic compound (cf. reviews on peroxides[1-5,91-97]):

$$RX + R'OOM \rightarrow ROOR' + MX \quad ,$$

R and R′ are organic or organoelemental radicals, X = Cl or Br, and M = Li, Na, or K.

In the preparation of peroxides stable against hydrolysis a hydrated salt obtained in the reaction of a hydroperoxide with a hydrated alkali hydroperoxide can be used[7,11,98]. The reaction takes place at 20°C or under gentle heating in an organic solvent in which the alkali halide is insoluble (hydrocarbon, alcohol, mixture of alcohol and ketone).[99] However, it must be taken into account that primary and secondary alcohols, and also ketones, are oxidised comparatively readily by salts of hydroperoxides[51,73].

Esters of peroxo-acids are obtained by the reaction of salts of hydroperoxides with acid chlorides[100-102].

The purest organometallic peroxides are obtained in the best yield from anhydrous salts formed in reaction between hydroperoxides and sodium[20-23] or potassium[25] amide, sodium hydride[18], and lithium t-butoxide[17]. The best solvents for making organometallic peroxides are hydrocarbons, which are the most inert to the initial compounds and to the peroxides obtained. Alcohol[103-105] can be used as the solvent when the initial organometallic compound and the peroxide product do not undergo alcoholysis. However, the salt obtained by the reaction of a hydroperoxide with sodium or potassium methoxide can contain a certain amount of alkoxide owing to the equilibrium[21].

When the organometallic compound is hydrolysed slightly the hydrated salt obtained by the reaction between a hydroperoxide and KOH in hydrocarbon medium is used. However, it was noted recently that the method based on the reaction of a hydroperoxide with a base (KOH, pyridine)[106,107] cannot be employed for obtaining large quantities of dialkyl t-butyl peroxophosphates owing to side-reactions[108]. The method using an anhydrous hydroperoxide salt is better.

Razuvaev and Fedotova[109] were the first to obtain an organomercury peroxide by the reaction:

$$C_6H_5HgCl + NaOOC(CH_3)_2C_6H_5 \rightarrow C_6H_5HgOOC(CH_3)_2C_6H_5 + NaCl \quad .$$

Other organomercury peroxides were obtained similarly[110-112]. When mercury(II) chloride reacts with ROONa in a mixture of benzene and ether, mercury bis(cumyl peroxide) is obtained[113], but with a peroxo-acid and NaOH in water the mercury salt of the peroxo-acid is obtained[114].

Razuvaev, Graevskii, and their coworkers[115-117] were also the first to obtain aluminium OP by the reaction:

$$(C_2H_5O)_2AlCl + NaOOC(CH_3)_2C_6H_5 \rightarrow (C_2H_5O)_2AlOOC(CH_3)_2C_6H_5 + NaCl \quad .$$

Boron OP[118,119] and an organothallium peroxide[120] have also been obtained similarly.

The preparation of the organometallic peroxides of Periodic Group IV elements was also described in detail in a review[121]. Salts of hydroperoxides have been used to obtain organometallic peroxides of silicon[19], germanium[21,122], tin[20,21,103-105,123], and lead[20,21] of the general formula R_3MOOR'. Thus the organosilicon peroxides R_3SiOOR' are obtained in especially good yield in the reaction of trialkyl- and triphenyl-chlorosilanes with an anhydrous salt R′OONa in an aprotic solvent[19]. The sodium salt of trimethylsilicon hydroperoxide, which can be obtained from a symmetrical peroxide undergoes analogous reactions[124,125]:

$$(CH_3)_3SiOOSi(CH_3)_3 + C_2H_5ONa \rightarrow (CH_3)_3SiOC_2H_5 + NaOOSi(CH_3)_3 \quad .$$

When silicon-containing acyl chlorides react with an anhydrous salt ROOLi in ether, esters of organosilicon peroxocarboxylic acids are obtained, in which the peroxide oxygen is separated from the heteroatom by a hydrocarbon moiety[126-131]:

$$R_3Si(CH_2)_nC(O)Cl + LiOOR' \rightarrow R_3Si(CH_2)_nC(O)OOR' + LiCl \quad ,$$
$$R{=}CH_3,\ C_2H_5,\ n{=}1,2,3; \quad R'{=}(CH_3)_3C,\ C_6H_5(CH_3)_2C \quad .$$

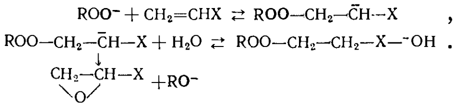
A large number of phosphorus[108,132-140], arsenic[141-143], and antimony[141-144] OP have been made by using alkali salts of hydroperoxides.

The interaction of ROOK with tetra-alkylammonium[145] and quanidinium[146,147] halides in methanol has been used to obtain salts of hydroperoxides and corresponding nitrogenous bases:

$$R_4NCl + KOOR' \rightarrow R_4NOOR' + KCl \quad ,$$
$$R = CH_3,\ C_2H_5,\ n\text{-}C_4H_9,\ R' = (CH_3)_3C,\ C_6H_5C(CH_3)_2 \quad ,$$
$$(RNH)_2C{=}NR \cdot HCl + KOOR' \rightarrow (RNH)_2C{=}NR \cdot HOOR' + KCl \quad .$$

Sym-triazine peroxides have been obtained by the reaction of salts of hydroperoxides with 2,4,6-trichloro-1,3,5-triazine.[148,149] The lithium salt of t-butyl hydroperoxide replaces only two chlorine atoms in the 2,4,6-trichloro-1,3,5-triazine molecule but under the action of the more reactive potassium salt of the hydroperoxide all three chlorine atoms are replaced by peroxide groups[149].

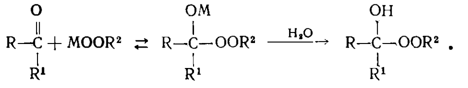
Organic peroxides can also be obtained by the addition of a peroxide anion to alkenes containing an electron-withdrawing substituent X.[150-152] A certain amount of epoxide is also formed:



$$ROO^- + CH_2{=}CHX \rightleftarrows ROO{-}CH_2{-}\bar{C}H{-}X \quad ,$$
$$ROO{-}CH_2{-}\bar{C}H{-}X + H_2O \rightleftarrows ROO{-}CH_2{-}CH_2{-}X{-}{}^-OH \quad .$$

Peroxoalkyl phosphonates are obtained by the reaction of salts of hydroperoxides with alkenyl phosphonates[153].

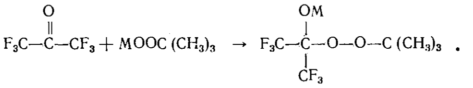
The reaction of salts of hydroperoxides with carbonyl compounds leads to α-hydroxyperoxides[51,76,154]:



$$R{-}C({=}O){-}R^1 + MOOR^2 \rightleftarrows R{-}C(OM)(R^1){-}OOR^2 \xrightarrow{H_2O} R{-}C(OH)(R^1){-}OOR^2 \quad .$$

$R = H$, alkyl; $M = Li, Na, K$

Fluorinated peroxides containing an alkali metal, which serve as initiators of the polymerisation of alkenes (especially fluoroalkenes), have been obtained in this way[155]:



$$F_3C{-}C({=}O){-}CF_3 + MOOC(CH_3)_3 \rightarrow F_3C{-}C(OM)(CF_3){-}O{-}O{-}C(CH_3)_3 \quad .$$

$M = Li, Na, K$

As already stated, when anhydrous alkali salts of hydroperoxides react with carbon dioxide percarbonates are obtained $R{-}O{-}O{-}C(O){-}OM$ where M = Li, Na, or K and R = cumyl[74,75].

Preparation of Hydroperoxides, Alcohols, and Other Oxygen-Containing Compounds

Salts of hydroperoxides are obtained when organolithium and organomagnesium compounds are oxidised by oxygen at −75°C,[15,16], when the salts are acidified the hydroperoxide is released. The yield can reach 75 to 85%.[16]

Decomposition of salts of hydroperoxides with the formation of free radicals is used for initiating the oxidation of hydrocarbons, for example, cumene to a hydroperoxide[156-159]. Phenol and acetone are obtained in the acid decomposition of cumyl hydroperoxide but the product from alkali splitting is 1-methyl-1-phenylethanol, which is dehydrated to α-methylstyrene[160].

The preparation of hydroperoxide salts is widely used in the separation of hydroperoxides from the reaction mixtures obtained by the oxidation of hydrocarbons and also for purifying hydroperoxides[160,161].

Alkali Organic Peroxides—Intermediate Products in the Production of Inorganic Peroxide Compounds of Alkali Metals

Alkali alkoxides of secondary alcohols are oxidised readily at 0–20°C with the formation of alkali metal inorganic peroxide compounds[37-39,162]. Depending upon the conditions (nature of the alkali metal, solvent, additive) an alkali metal hydroperoxide, peroxide, or superoxide is formed. The intermediate oxidation products are the unstable alkali salts of hydroperoxides of secondary alcohols $R_2C(OH)OONa$ and $R_2C(ONa)OONa$, which decompose into the ketone and inorganic peroxide compound. The greatest interest is in the production of sodium superoxide NaO_2 in the catalytic oxidation of sodium under mild condition in aprotic polar organic solvents[163,164]. The catalysts are aromatic ketones, hydrocarbons, or nitrogen-containing compounds, which easily form organic (ketyl or complex) compounds with an alkali metal. During its oxidation the superoxide is formed and the catalyst is regenerated. This preparation of NaO_2 can be carried out at 0–20°C and atmospheric pressure. In industry NaO_2 is obtained by the oxidation of Na_2O_2 at high pressures and temperature,[162].

Other Regions of Use

Salts of hydroperoxides are used as initiators of the polymerisation of alkenes[165]. The polymerisation of ethylene is carried out at 145–175°C and a pressure of 200–1000 at. in a medium of alcohol, hydrocarbon, or water. Copolymers of ethylene with styrene, α-methylstyrene, methyl vinyl ketone, vinylpyridine, acrylic and methacrylic acids, methyl and ethyl acrylate, or methacrylate can be obtained and also these individual vinyl compounds can be polymerised[165]. Salts of hydroperoxides were recently proposed for use as components of detergents[166].

Unlike the lithium, sodium, and potassium OP, there have been very few studies of the corresponding magnesium and alkaline earth compounds. This seems to be due to their insolubility in organic solvents. We know of only a few papers which describe the preparation of the OP of these metals by the reaction of hydroperoxides (or peroxo-acids) with the corresponding bases (oxide[10], hydride[18], organomagnesium compound[167]). Thus when hydroperoxides react with strontium or barium oxides the salts $M[OOC(CH_3)_3]_2$ are obtained[10], where M = Sr or Ba. Peracetates have been obtained in the reaction between calcium and barium hydrides with the peroxoacid in tetrahydrofuran[18].

The reaction of the organomagnesium compounds $ROMgC_5H_{11}$, $ROMgR^1$ and R^1_2Mg with cumyl hydroperoxide or with hydrogen peroxide in ether at 0°C the magnesium OP $ROMgOOR^2$, $ROMgOOMgOR$, and $R^1MgOOMgR^1$, where $R = (CH_3)_3C$, $R^1 = C_6H_5$, and $R^2 = C_6H_5C(CH_3)_2$, are obtained[167].

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State of the Theory of Iso-free Volume and Glass Formation in Amorphous Polymers

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Methods of determining the free volume fraction of polymers at the glass formation temperature and the concept according to which all polymers have a universal free volume fraction at the glass point are considered critically. The concept of iso-free volume in glass formation can be regarded only as a rough approximation and the free volume fraction is a function of several variables including the flexibility of the polymeric chain and the nature of the molecular packing. The development of the theory of glass formation by amorphous polymers on the basis of the free volume concept is considered and it is shown that a free volume distribution function has to be introduced for the correct description of the process. Conclusions are drawn concerning the inapplicability of the iso-free volume concept for describing glass formation processes in amorphous polymers. The possibilities of a more adequate description of glass formation are discussed. 69 references.

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I. THE FREE VOLUME CONCEPT AND ITS CONNECTION WITH GLASS FORMATION BY AMORPHOUS POLYMERS

Many of the properties of high- and low-molecular-weight substances (viscosity, thermal, mechanical, relaxation, etc.) and processes in them (diffusion, permeability, sorbtion) are connected with the molecular mobility and structure of these compounds, determined by the degree of ordering of the molecules. The structure and properties of such substances can be described from the thermodynamic viewpoint through configuration free energy[1] and enthalpy[2]. However, phenomenologically one of the most convenient ideas is excess or free volume. According to Covacs[3], free volume is a characteristic of the disorder of the structure and determines the rate of molecular rearrangements. This characteristic is closely connected with the configuration mobility of a liquid and its thermodynamic parameters and could be classified among the fundamental characteristics of the liquid state if the existing theory could give a precise definition of the concept of free volume and methods for its determination.

Actually, the most important properties of liquids, and above all viscosity and capability of glass formation, show they contain a free volume, which can be represented as holes or vacancies of approximately molecular dimensions, rated to the irregular packing of the molecules. Although, according to Ferry[4], the free volume per 1 g substance, v_f, is very difficult to determine, it is a useful semiquantitative concept. In particular, the greater part of the thermal expansion coefficient of liquids is due to an increase in the free volume, whereas its lesser part is linked with the anharmonicity of the relation between potential energy and the interatomic or molecular distances.

The concept of free volume is based on the Doolittle empirical equation[5], which connects viscosity with specific free volume:

$$\ln \eta = a + b/f, \tag{1}$$

where a and b are constants,

$$f = (v - v_0)/v, \tag{2}$$

v and v_0 are the actual and occupied volumes of the liquid at temperature T:

$$v - v_0 = v_f.$$

By occupied volume is meant the proper total volume of the molecules.

The concept of free volume proved very useful and was employed for the theoretical description of many processes in liquids, including processes in polymers. A theory of the diffusion of low-molecular substances in polymers[6,7], a theory of thermal conductivity[8], a theory of solutions and solubility of polymers[9], etc. were developed on the basis of the free volume concept. However, the free volume concept was used most extensively in the theory of viscoelastic properties of polymers, developed by Williams, Landell, and Ferry, and stated in detail in Ferry's monograph[4]. According to this theory, the change in the viscosity of a liquid with temperature in the range from T_g to T can be described with the aid of a normalisation coefficient

$$a_T = \eta_T/\eta_{T_g}.$$

By using Doolittle's equation (1) connecting the viscosity and the free volume, we can obtain:

$$\lg a_T = \frac{-(B/2{,}303 f_g)(T - T_g)}{f_g/\alpha_f + T - T_g}, \tag{3}$$

where f_g is the free volume fraction at T_g, B a constant, and α_f is regarded as a coefficient for the increase in free volume (see below). The values of f_g found experimentally according to this equation are the same (0.025 ± 0.003) for most polymers.

Bueche[10] further developed the theory of viscoelastic properties based on the free volume concept, by starting from the assumption that some element of the structure can be displaced when the fraction of local relative free volume f exceeds some critical value f_c. The frequency ν of the corresponding molecular process can be expressed by the equation

$$\nu = \nu_g \exp[-Nf_c(1/f - 1/f_g)],$$

where ν_g is the frequency at T_g. When (as will be considered below)

$$f = f_g + \alpha_f(T - T_g), \tag{4}$$

then

$$\ln(\nu/\nu_g) = \frac{Nf_c/f_g\,(T - T_g)}{T - T_g + f_g/f}\,.$$

This equation is identical in form with Eqn. (3).

Simha and Boyer[11] were the first to use the free volume concept in considering processes of glass formation in amorphous polymers. By analogy with Eqn. (2) they assumed that the free volume fraction at the glass formation temperature is

$$f_g = (v_g - v_{0g})/v_g = 1 - v_{0g}/v_g, \tag{5}$$

where v_g and v_{0g} are the actual volume and the volume occupied by the molecules, at T_g. On assuming that the specific free volume is a linear function of temperature then clearly condition (4) will be observed, at which

$$\alpha_f = (\partial f/\partial T)_p \simeq 1/v\,[(\partial v/\partial T) - (\partial v_0/\partial T)]_p. \tag{6}$$

Eqn. (5) can also be written in the form

$$f_g = [v_g - v_{0l}(1 + \alpha_g T_g)]/v_g \simeq [v_g - v_{0l}(1 + \alpha_g T_g)]/v_{0l},$$

where v_{0l} is the occupied volume in the initial state, $T = 0$, α_g the coefficient of expansion of the vitrified liquid below T_g. In this definition, f_g is found from the difference between the actual volume and the volume which the liquid would have at the glass formation temperature were the volume of the liquid v_{0l} to increase with the expansion coefficient α_g characteristic of the vitreous state. Then the actual volume at the glass point is

$$v_g = v_{0l}(1 + \alpha_g T_g),$$

and the free volume fraction equals

$$f_g = [v_{0l}(1 + \alpha_l T_g) - v_{0l}(1 + \alpha_g T_g)]/v_{0l}.$$

From this relation we have[11]

$$(\alpha_l - \alpha_g)T_g = f_g = K_1. \tag{7}$$

In 1950 Fox and Flory[12] introduced the concept according to which the glass formation temperature corresponds to the state of iso-free volume. This concept has been developed[13,14], is used widely, and with slight modification provides a basis for various theories of glass formation[11,15,16]. The constant value found by Simha and Boyer[11] for K_1 for various polymers served as confirmation of the definition of iso-free volume as the volume corresponding to the glass formation temperature.

If it is also assumed that at T_g the partial free volume is constant for all polymers, then having determined this volume as

$$K_2 = (v - v_{0l})/v,$$

it can be shown that

$$K_2 = \alpha_l T_g.$$

Actually, K_2 can be written as:

$$K_2 = \frac{v_{0l}(1 + \alpha_l T) - v_{0l}}{v_{0l}(1 + \alpha_l T)} = \frac{\alpha_l T}{1 + \alpha_l T} \simeq \alpha_l T.$$

Eqn. (6) also suggests that the ratio of the linearly extrapolated volumes v_{0g} and v_{0l} at $T = 0$, K is almost independent of the nature of the polymer. Then

$$v_{0g}/v_g = (1 + \alpha_l T_g)/(1 + \alpha_g T_g) = 1 + (\alpha_l - \alpha_g)T_g - \alpha_g(\alpha_l - \alpha_g)T^2 \simeq 1 + K_1.$$

It was found that $K_1 = 0.113$ and $K_2 = 0.164$ for most of the polymers. Hence the expressions for K_1 and K_2 characterise corresponding states in the free volume terms.

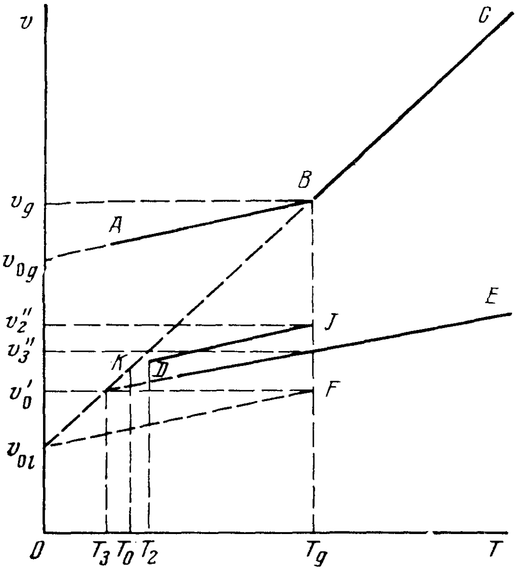

Figure 1. Scheme for the calculation of free volume characteristics in various theories.

II. METHODS OF CALCULATING THE FREE VOLUME FRACTION AT THE GLASS FORMATION TEMPERATURE

In the definitions considered above the free volume fraction depends on which volume was taken as the initial value for the state, that is, on the method of calculation. Even in this very fact some vagueness is introduced into the physical significance of free volume. In this connection, we will consider various computational methods of determining the initial volume, since on this depends the calculated fraction of the free volume at T_g.

Fig. 1 shows schematically the variation of specific volume with temperature. Here the line *ABC* represents the curve of the change in actual volume of an amorphous polymer during passage through T_g. The segment *AB* (with slope α_g) corresponds to the vitreous stage, segment *BC* (with slope α_l) to the highly elastic state. The straight line *DE* parallel to *AB* corresponds to a change in volume in the crystalline state if it is assumed (as is usual[11,17]) that the coefficients of thermal expansion in the vitreous (α_g) and crystalline (α_c) states are equal. On extrapolating the segment *BC* to 0 K, the value of v_{0l} is obtained, and extrapolating *AB* gives the value of v_{0g}. Hence the free volume fraction according to Simha and Boyer is determined (the segment $BF = \Delta\alpha \cdot T_g$, is the occupied volume v_0').

According to Williams–Landell–Ferry, the occupied volume is taken to be the quantity v_2'' obtainable by extrapolation of the volume of the liquid corresponding to some temperature T_2, determinable from the viscometric results[15,18] parallel to AB up to T_g (the segment BJ). According to Tobolsky's determination[19], the occupied volume v_3'', corresponds to the volume of the specimen in the crystalline state at T_g. According to Miller[20], the free volume is determined from the relation to the temperature T_0 entering into the Fogel equation for the temperature dependence of viscosity. Point K represents a hypothetical volume larger than for the crystalline state, but less than for the glass at the same temperature. Consequently, the free volume here is somewhat greater than that determined according to Williams–Landell–Ferry.

According to Miller,

$$v_f = v - v_0 = 0 \quad \text{at} \quad T = T_0.$$

Then at any other temperature

$$v_f = \Delta\alpha\,(T - T_0), \tag{8}$$

where

$$\Delta\alpha = \alpha_l - \alpha_g.$$

Correspondingly at T_g

$$v_f = \Delta\alpha\,(T_g - T_0). \tag{9}$$

According to the Simha–Boyer theory,

$$\Delta\alpha \cdot T_g = K_1$$

By equating the $\Delta\alpha$ in expressions (8) and (9) we can obtain the following relation:

$$K_1/(v_f)_{T_g} = T_g/(T_g - T_0).$$

Covacs[3] gives yet another definition of the free volume fraction. Since the extrapolatable volume of the supercooled liquid reaches the volume of the crystalline state v_c at some temperature $T_c > 0$ K this critical temperature can be compared with $T_{g,\infty}$ the limiting temperature of glass formation at infinitely slow cooling, assuming that in the crystalline state the free volume is zero. Then the quantity f_g defined according to Doolittle can be compared with the $f_{g,c}$ characterising the excess free volume of a glass compared with the crystal:

$$f_{g,c} = (v_g - v_c)/v_g.$$

The comparison of f_g and f_c for amorphous polymers is naturally difficult since the volume v_c can be found experimentally only when the polymer is capable of crystallising. In this approach it is assumed that $\alpha_c \simeq \alpha_g$; thus for polystyrene usually $f_{g,c} = 2f_g$. It is usually assumed that the free volume fraction varies with the temperature in accordance with relation (4), where the coefficient of expansion is determined by Eqn. (6). According to Ferry[4], when the macroscopic coefficient of expansion α_l at temperatures higher than T_g reflects the appearance of free volume, then $\alpha_f = \alpha_l - \alpha_g = \Delta\alpha$ should apply. Actually, the $\Delta\alpha$ found experimentally correspond well with the values of α_j calculated from the Williams–Landell–Ferry theory. In addition, we wish to emphasise that the actual value of $\Delta\alpha = \alpha_f = \alpha_l - \alpha_g$ is not the coefficient of expansion of the free volume as such, but the temperature coefficient of the free volume fraction. Elementary calculation shows that the actual increase in volume above T_g cannot be equal to $v_g\alpha_f(T - T_g)$, if v_g is determined by starting from the actual specific volume at T_c and the known f_g.

As is evident from what has been stated, irrespective of the method of estimating the occupied volume adopted in the various theories the free volume fraction is always determined by Eqn. (5) and consequently the values of f_g calculated by the various methods do not agree with one another. This emphasises that this is not an absolute quantity and shows the need to regard it only as a convenient parameter for describing the properties of a liquid. Even in 1963, Boyer[17] noted that the free volume at T_g is constant only under certain conditions and varies with the molecular mass, the degree of cross-linking, and other characteristics of the polymer.

III. THERMODYNAMIC AND MOLECULAR EXAMINATION OF THE FREE VOLUME CONCEPT

Hirai and Eyring[21] found that the quantity $\Delta\alpha . T_g$ depends on ϵ_h, the energy of hole formation:

$$\Delta\alpha \cdot T_g = (\varepsilon_h/RT_g)\exp[-(\varepsilon_h/RT)].$$

By taking $f_g = 0.02$, they theoretically calculated the value $\Delta\alpha . T_g = 0.08$. According to their views:

$$\varepsilon_h/RT_g \simeq -\ln f_g.$$

Since ϵ_h is proportional to the cohesion energy density E, it can be shown that

$$T_g = [\Delta H' + ME]/(-R\ln f_g),$$

where

$$\Delta H' = \Delta H_f - \Delta H_h,$$

ΔH_f is the heat of fusion, ΔH_h is that part of the heat of fusion associated with the "fusion" of the holes, and M is a constant.

The free volume concept as applied to processes of glass formation was developed further in Miller's work[20,22]. The basis of Miller's ideas was that if any excess function

$$\Delta X\,(\text{liquid}) - X\,(\text{crystal})$$

is extrapolated to zero at some temperature exceeding 0 K;[22] these temperatures correspond to the excess volume equalling zero. Miller showed that the excess entropy and excess volume are reduced to zero at the same temperature, corresponding to the temperature T_0 in the Fogel equation. According to Miller, the coefficient A in the Fogel equation:

$$\lg\eta = \lg A + B(T - T_0)$$

is connected with the weighed mean number of the bonds in the macromolecule z_w by the ratio:

$$\lg A = \lg K + 3.4\lg z_w.$$

From these two equations, at T_g:

$$\lg\eta_g = \lg K + 3.4\lg z_w + B(T_g - T_0).$$

The parameters for the vinyl polymers give the relation $B/(T_g - T_0) \simeq 15$. From the standpoint of ideas about free volume:

$$\lg\eta \propto b/(v_f)_{T_g}.$$

From this it can be shown that:

$$(v_f)_{T_g}/b = (T_g - T_0)/2, \quad 3b \simeq 0.029.$$

This corresponds to the value given by the Williams–Landell–Ferry theory. Hence in principle the idea of iso-free volume follows directly from the viscosimetric measurements. The difference in the definition of the free volume according to Miller from the Simha–Boyer definition is that

$$(v_f)_{T_g} = \Delta\alpha\,(T_g - T_0) \approx 0.11 - \Delta\alpha T_0,$$

and the last term is not constant for different vinyl monomers. Hence

$$0.11/(v_f)_{T_g} = T_g/(T_g - T_0).$$

Miller[23] suggested that the right-hand side of this equation equals the number of monomeric units at T_g in the "cooperative unit", z_g^*. Then

$$z_g^*(v_f)_{T_g} = 0.11.$$

This condition is another criterion of the glass–liquid change. According to this determination the greater the free volume fraction left for segmental motion movement, the less the "cooperative unit" which is required for this movement to maintain the state of isomobility at T_g. An analogous concept was proposed by Bueche[24], who considered the variation in the free volume and greatest free volume f_c, necessary for the movement of a group of n units.

From what has been stated above, Miller assumes[25] that there is a relation

$$z_g^* S_c = A,$$

where S_c is the configuration entropy. Miller was the first to present the problem of whether the concept of free volume reflects the configuration entropy changes which are taken into account by the parameter z_g^*, the cooperative unit for segmental motion.

It is generally accepted that the viscous flow of polymeric liquids is connected with the rotation of the segments of chains, that is, with conformation entropy. From this point of view Miller assumes that the Simha–Boyer equation is incorrect, since according to it the relative free volume is zero at 0 K, and not at $T = T_0$; under this condition K_1 should be constant. Hence we here again encounter the fact that the constancy or non-constancy of the free volume fraction at T_g depends on how this fraction is expressed. Subsequently, from a consideration of the viscosity of melts at various temperatures and pressures Miller[26] concluded that the mobility of polymeric liquids depends to a much greater extent on the thermal factor than on the volume and that any versions of the free volume theory connecting the viscosity with the relative free volume fraction are inapplicable in real examples.

In all the examples considered above the concept of free volume is based on the position that free volume plays the main part in the properties of a liquid. Meanwhile Miller[27] notes correctly that the whole theory of liquids presumes that the intermolecular potential energy $U(r)$ is an important factor, which determines molecular friction. At the same time the free volume fraction f is connected solely with the intermolecular distance; all the equations which include f are incomplete owing to the absence of an energy term from them. According to Miller[27], for a hypothetical liquid at 0 K the kinetic energy is zero and the volume v_0 is determined exclusively by the potential energy of interaction U_0. The value of U_0 should be closely connected with the vaporisation energy ϵ_0 at 0 K. Hence the parameters ϵ_0, v_0, and the "zero" cohesion energy density, $(\epsilon_0/v_0)_0$, provide a basis for determining the free volume, $v_f = v - v_0$.

There has been shown to be an empirical relation connecting the compressibility coefficient of the liquid β with the free volume fraction:

$$-\beta \simeq kf^2(1-f).$$

Here $\beta = 1/v(\mathrm{d}v/\mathrm{d}p)_\mathrm{T}$ at $p = 1$ atm. It was suggested that

$$-f^2(1-f) \approx 5\beta\,(\varepsilon/v)_0,$$

or

$$-f^2 \approx 5\beta\varepsilon_0/v.$$

In this consideration, energetic and volume factors are introduced into the equations which describe the compressibility of the liquid, and from the standpoint of molecular theory these factors essentially determine the properties of liquids.

On the other hand, in a series of papers after that of Hirai and Eyring[21] ideas have been developed concerning the energies of formation of unit free volume or of 1 mole of holes. The latest of these views was developed by Kanig[28], who simultaneously introduced a refinement into the concept and definition of the free volume. By starting from the position of Frenkel', [29] Kanig divides the free volume into two parts, one of which is determined solely by the thermal vibrations of the atoms in the lattice of a real crystal or liquid, and the other consists of the vacancies or holes proper in the liquid, which make possible an exchange of particles with the sites, that is, ensure the very existence of the liquid state. For this example, new definitions of the free volume fractions are introduced:

$$\varphi_{f_1} = \frac{N_1 v_{f_1}}{N_1 v_{f_1} + N_2 v_{f_2}},$$

$$\varphi_{f_2} = \frac{N_2 v_{f_2}}{N_1 v_{f_1} + N_2 v_{f_2}},$$

where N_1 and N_2 are the numbers of holes and molecules in the system, v_{f_2} is the volume determined by the thermal vibrations, and v_{f_1} the volume determined by the holes. These expressions involve the ratio of the proper volume of the vacancies and the "volume of the vibrations" to the total free volume, as distinct from the usual definition, which includes the ratio of the free volume to the total volume:

$$f_g = \varphi_1^* = \frac{v_1^*}{v_1^* + v_2^*},$$

where v_1^* is the partial volume of the holes, and v_2^* the partial volume of the molecules at T_g, including the volume due to the thermal vibrations. In the first instance, by starting from the total dilatometric curve it can be shown that (Fig. 2) the segment BE represents the quantity

$$N_2 v_{f_2} = T_g \mathrm{d}v_g/\mathrm{d}T,$$

and the segment EL the volume of the vacancies

$$N_1 v_{f_1} = T_g \mathrm{d}v_l/\mathrm{d}T - T_g \mathrm{d}v_g/dT.$$

Hence the free volume is defined as the segment BL:

$$N_1 v_{f_1} + N_2 v_{f_2} = T_g\,\mathrm{d}\,v_l/\mathrm{d}\,T.$$

From many experimental results Kanig deduced that the free volume fraction at T_g usually determined is not constant and that for characteristics of the state of iso-free volume it is more desirable to use the quantities φ_{f_1} and φ_{f_2}, referred to the glass formation temperature, $\varphi_{f_1}^*$ and $\varphi_{f_2}^*$. Then from Fig. 2,

$$\varphi_{f_1}^* = \frac{v_{0g} - v_{0l}}{v_g - v_l},$$

$$\varphi_{f_2}^* = \frac{v_g - v_{0g}}{v_g - v_{0l}}.$$

Actually, it appeared that the quantities $\varphi_{f_1}^* \simeq 0.64$ and $\varphi_{f_2}^* \simeq 0.36$ are less different for different polymers than is the quantity usually determined. The fractions $\varphi_{f_1}^*$ and $\varphi_{f_2}^*$ are, according to Kanig, constants independent of the nature of the substance and which characterise the corresponding states at the glass formation temperature. The relations given show that at the glass formation temperature there should be a constant ratio between the volume of the vacancies and the volume determined by the thermal vibrations, at which translational motion of the molecules becomes possible. In particular, these quantities enter into the equation describing T_g as a function of the degree of polymerisation.

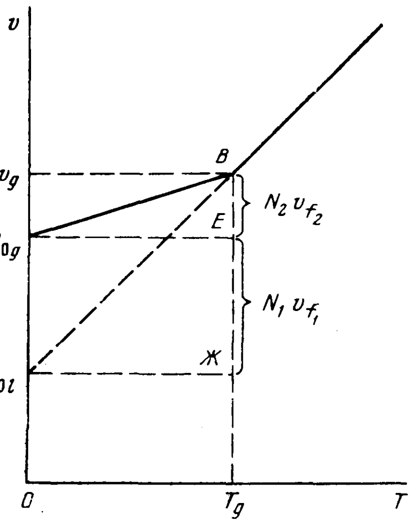

Figure 2. Scheme for the calculation of free volume characteristics after Kanig.

Kanig[30] has introduced allowance for the temperature dependence of the quantity $\varphi_{f_1}^*$, determined from the results for the free volume fraction defined by him above, Below T_g, as the temperature is reduced $\varphi_{f_1}^*$ increases owing to the decrease in the volume due to the vibrations when there is "freezing" of the volume of the vacancies. Above T_g, there is an increase in $\varphi_{f_1}^*$, due to the increase in the volume of the vacancies being faster than the increase in the volume due to the vibrations. At $T = T_g$ the quantity $\varphi_{f_1}^*$ is a minimum. From the condition for an extremum $d\varphi/dT = 0$ it can be found that $\varphi_{f_1}^* = (\alpha_l - \alpha_g)/\alpha_l$. This actually gives the same value for $\varphi_{f_1}^*$, also without allowance for the temperature coefficient. However, Kanig introduces a refinement, according to which for the corresponding states at T_g there are extremal values $\varphi_{f_1}^*$ and $\varphi_{f_2}^*$, which are constants irrespective of the nature of the substance.

Experimental verification of the relations obtained by Kanig and given by him[31] showed that the traditional definition of the free volume fraction according to Fox and Flory or according to Williams, Landell, and Ferry can lead to the best agreement with experiment when allowance is made for the geometric parameter α. Kanig[31] began from the fact that the partial free volume $\varphi_1^* = f_g$ at the temperature of glass formation, as stated above, can be regarded only to a rough approximation as a constant, the mean value of which corresponds to the universal value obtained by the Williams-Lindell-Ferry theory. The real picture is that polymers with more flexible chains exhibit lower values of φ_1^* than polymers with rigid chains. Consequently, Kanig considers it necessary to introduce a parameter a for a characteristic of the corresponding states. The basis for such introduction is the thermodynamic consideration of a polymer melt as a mixture of chain molecules *2* with holes *1* assuming that the melt is saturated with holes at any temperature. By the introduction into the consideration of the energies of interaction in pairs W_{11} (hole–hole), W_{21} (polymer–hole), and W_{22} (polymer–polymer) the partial thermodynamic characteristics of the dilution of the melt with holes can be calculated. The following parameters enter into these expressions: O_1 the contact surfaces of a mole of holes, and O_2 the contact surfaces of a mole of repeating units of the polymer. For the displacement of n_2 moles (links) of the polymeric chains and n_1 moles of holes it can be shown that

$$1/\varphi_{f_1} \simeq \frac{n_2 O_2}{n_1 O_2} \simeq \frac{O_2/v_2}{O_2/v_1} \frac{n_2 v_2}{n_1 v_1} \simeq \frac{1}{a} \cdot \frac{1}{\varphi_1},$$

if it is assumed that

$$n_1 v_1 \ll n_2 v_2$$

and

$$\varphi_1 = \frac{n_1 v_1}{n_1 v_1 + n_2 v_2}, \quad \varphi_2 = 1 - \varphi_1,$$

where v_1 and v_2 are the molar volumes of the holes and links, and $a = (O_1/v_1)/(O_2/v_2)$. Here a has the physical significance of a parameter determining the size and form of the macromolecules. Kanig assumes that this parameter is more real for the description of the molecule than the coordination number usually employed. From this he deduces an expression for the glass formation temperature:

$$T_g = -\frac{(1 - a\varphi_1^*) H_{0i}^*}{R(\ln \varphi_1^* + \varphi_2^*)} = -\frac{\Delta H_1^*}{R(\ln \varphi_1^* + \varphi_2^*)},$$

or

$$T_g = K(\varphi_1^*) \Delta H_1^*,$$

where

$$H_{0i} = O_1 \cdot \Delta W_{12}, \quad \Delta W_{12} = -{}^1/_2 (W_{22} + W_{11});$$

the asterisk shows that all the values relate to T_g. Hence the glass formation temperature is related to the free volume and the energy of formation of the holes, and consequently depends on the intermolecular energy ΔW_{12} and the geometric factor a. Starting from the method of consideration used, Kanig found[31], that

$$T_g \Delta\alpha^* = K(\varphi_1^*, a) = \frac{\varphi_1^*}{2a_1\varphi_1^* + (\varphi_2^*)^2/(\ln \varphi_1^* + \varphi_2^*)},$$

where $\Delta\alpha^*$ is the difference between the expansion coefficients above and below T_g. Clearly, this equation would correspond to the Simha–Boyer empirical equation were the quantity K to be constant, that is, in accordance with the iso-free volume theory, were constant and the value of the parameter a would be the same for all polymers.

Kanig's approach has the advantage in comparison with the others that there is a relation between φ_1^* and a with those parameters determined experimentally, such as $\Delta\alpha$ and ΔC_p (change in heat capacity on going from glass to liquid) and also with ϵ_g the molar energy of cohesion at T_g. This allows φ_1^* and a to be calculated from the experimental results. The mean values thus determined with allowance for the concept of iso-free volume are:

$$\bar{\varphi}_1^* = 0.0235 \pm 0.0050$$

(mean error ± 21%) and

$$\bar{a} = 3.15 \pm 0.35$$

(mean error ±11%). On the one hand, the correspondence found for the universal value in the Williams–Landell–Ferry theory indicates that the free volume is that volume determined by the holes; on the other hand, from what has been stated it seems that the Simha–Boyer constant is a complex function of φ_1^* and a. The obtaining of an experimental relation between

$$\frac{\varphi_1^*}{2a\varphi_1^* + \varphi_2^{*2}/(\ln \varphi_1^* + \varphi_2^*)} \cdot \frac{1}{T_g}$$

shows a significant departure from linearity. φ_1^* not being constant shows that the iso-free volume concept is not strictly true.

IV. STATE OF THE ISO-FREE VOLUME DURING GLASS FORMATION

The idea that the free volume fraction, determined experimentally using various equations, at the glass formation temperature depends on the type of molecular movements was first expressed in 1967 [32,33] in connection with results on the relaxation of volume for various polymeric systems. Calculations made on the basis of curves for finding equilibrium volume[32,33] allowed the relaxation time to be determined for different temperatures and then the free volume fraction at T_g was determined by the equation of the Williams–Landell–Ferry theory from the calculated quantities a_T and the $\Delta\alpha$ found.

On accepting the validity of the main position of the theory concerning the universal dependence of the coefficient of reduction a_T on the difference $T - T_g$, f_g can be determined from the results for $\Delta\alpha$ and the theoretical values of a_T calculated from the universal values of the coefficients C_1^g and C_2^g of the Williams–Landell–Ferry theory. The value found in this calculation corresponds to the universal one. However, when experimental values of a_T, and not theoretical ones, are used, the calculated free volume fraction, by remaining constant, will be significantly higher than the universal value and be $f_g = 0.08$–0.09. In considering this fact it is necessary to take into account that the value of f_g in the Williams–Landell–Ferry theory comes from results on dynamic mechanical properties, when relaxation processes are connected with the appearance of segmental mobility. In this instance the value of f_g for many polymers is close to universal, since it corresponds to the size of the holes necessary for the migrations of small structural units which determine the relaxation properties under these experimental conditions. However, it was found[33,34] that in polymers there are isophase transformations connected with the mobility of the structural units larger than statistical segments up to the processes which determine the mobility of the supermolecular formations. It is quite evident that the motion of the large structural elements requires a large hole dimension or a large free volume. It must therefore be assumed that in investigating various relaxation mechanisms the free volume fraction needed for the migrations of structural units of various dimensions can be determined. This also follows from other results[32,33] corresponding to the relaxation process with long periods, that is, with kinetic units of large dimensions. It is also quite evident that at the same density of molecular packing (volume of intermolecular vacancies) the actual free volume necessary for effecting one motion or another will be determined by the nature of these movements.

Actually, depending upon the type of molecular motion and the size of the corresponding movement of the kinetic unit the mobility can appear only at a definite value of the free volume, which therefore will depend on the type of the molecular motions. When the free volume is sufficient for the motion of relatively small structural units, for example, of segments, but insufficient for the motion of larger segments of the chains or of the chains as independent kinetic units, then the well-known non-correspondence between the values of T_g determined by different methods occurs. The same conclusion was reached by Sanchez[35], who found theoretically that the mean size of the holes increases with T_g. He assumes that this is connected with the higher T_g for polymers having more rigid chains. The packing of the rigid chains cannot be so compact as that of flexible chains, as a result of which the mean size of the holes increases. For example, for low-molecular-weight compounds the free volume fraction at T_g is less than for polymers, which is regarded as the result of the greater mobility of small molecules, for the realisation of which a smaller free volume is required. According to Mandelkern and coworkers[36], the Simha–Boyer rule should not be observed at all, since the $\Delta\alpha$ for various systems in which T_g can differ significantly lie within narrow limits, $(2.5$–$4.0) \times 10^{-1}$ K^{-1}. However, Simha and Boyer[37] consider such a conclusion erroneous owing to the incorrect treatment of the experimental results.

The limitations of the picture predicted within the framework of the Simha–Boyer theory lead to a search for new ways of improving it. It was carried out by Simha and Weil[38] who allowed for the temperature dependence of the coefficients α_l and α_g, which led to the need for extrapolating the volumes for the liquids to temperature below T_g with the aid of non-linear functions connecting volume and temperature. Such a consideration is based mainly on the fact that in a series of polymers with increasing side-chain length there is a systematic decrease in $\Delta\alpha \cdot T_g$, which suggests that there should be a considerable decrease in f_g in such systems.

According to Simha and Weil[38] there is a need to reconsider the postulate of free volume at T_g. On taking into account the temperature dependence of α_l and α_g, Simha and Weil[38] gave the following alternative expression for the free volume fraction:

$$(v_f)_{T_g} = 1 - \exp\left[-\int_0^{T_g} (\alpha_l - \alpha_g)\,\mathrm{d}T\right] \equiv (v_{0g} - v_{0l})/v_{0g}, \tag{10}$$

where v_{0l} and v_{0g} are the experimental and absolute zero volumes of the liquid and glass corresponding to the non-linear functions of the temperature dependence of both the expansion coefficients. Hence v_f is independent of temperature in the range $0 \leqslant T \leqslant T_g$, since the second identity is observed in this range of temperatures. Hence v_f can be regarded as a characteristic of the packing density of the glass at absolute zero. The first equality can be formally extended to the range $T > T_g$ by extending the upper limit of integration, which requires extrapolation of the vitreous state into the liquid region.

On the other hand, the occupied volume is simply v_{0l}, and hence

$$(v_f)_{T_g} = 1 - \exp\left[-\int_0^{T_g} \alpha_l \mathrm{d}T\right] \equiv (v - v_{0l})/v. \qquad (11)$$

Eqns. (10) and (11) give the most general expression for the Simha–Boyer rule. Simha and Weil[38] showed that since $\alpha \leqslant 8 \times 10^{-4}$ K^{-1} and $T_g < 5 \times 10^2$ K, for most of the polymers the exponents can be replaced by a series yielding

$$(v_f)_{T_g} \approx \int_0^{T_g} (\alpha_l - \alpha_g)\,\mathrm{d}T\left[1 - {}^1/_2\int_0^{T_g} (\alpha_l - \alpha_g)\,\mathrm{d}T\right]$$

and

$$(v_f)_{T_g} \approx \int_0^{T_g} \alpha_l \mathrm{d}T\left[1 - {}^1/_2\int_0^{T_g} \alpha_l \mathrm{d}T\right].$$

From the first equation, by neglecting the quadratic terms, we find that

$$(\alpha_l - \alpha_g)\,T_g \approx (v_f)_{T_g} + [\alpha_l n/(n+1) - \alpha_g m/(m+1)]\,T_g,$$

where α_l and α_g should be taken at T_g; n and m are constants. Hence the constancy of the left-hand part of the last equation does not signify that the free volume is constant, but quite the contrary. Since Eqns. (10) and (11) involve integration of the function $\alpha_l(T)$ over the range $0 \leqslant T \leqslant T_g$, not realisable experimentally, Simha and Weil give a method for the necessary extrapolation using reduced functions of temperature and pressure. Application of Eqn. (11) to the experimental results showed that there is a systematic decrease in the product $(\alpha_l - \alpha_g)T_g$ as the length of the linear side-chains of the polymers in the methacrylate series is increased. The experimental results also showed that the value of $(v_{0g} - v_{0l})/v_{0g}$ is not constant at T_g, whereas the ratio $(v - v_{0l})/v$ at T_g is comparatively stable. It was found that the main part of the discrepancies between the f_g for the individual systems at T_g is connected with the contribution of the vitreous rate to the free volume.

The change in the value of f_g for the various polymers can be significantly less when allowance is made for the non-linear temperature dependence of the specific volume of the polymer in the liquid and vitreous states. The decrease in f_g as the temperature is reduced also follows from Moacanin and Simha[39], who considered the entropy of mixing of holes and segments with allowance for the temperature dependence of the hole concentration needed for the minimisation of the free energy. The temperature T_2 at which the system is in equilibrium and the product $\Delta\alpha \cdot T_2$ in the Gibbs–DiMarzio theory[40] are functions only of the free volume v_g. The constancy of the product $\Delta\alpha \cdot T_2$ at $T = T_2$ corresponds to the constancy of $\Delta\alpha \cdot T_g$, if the temperature T_2 is proportional to T_g.

The results described above suggest that the concept of iso-free volume at T_g cannot be considered as proved and it is disproved by new experimental results. Consequently several papers[27,30] suggest that at T_g the liquid and polymer are not in a state of iso-free volume but in a state of iso-viscosity (the iso-viscous state).

In connection with this a modification of the Simha–Boyer rule was proposed, which can be expressed in the form[41]:

$$\frac{{}^1/_2\,[(\mathrm{d}v/\mathrm{d}T)_l + (\mathrm{d}v/\mathrm{d}T)_g]\,T_g}{v_g} = K_3.$$

The constant K_3 depends upon the type of bond in the main chain of the polymer and is constant for each class of polymer. Ellerstein[41] assumes that the physical interpretation of this equation can be combined with the concept of iso-free volume. However, in practice the introduction of this correction implies, as we assume, a departure from the concept of iso-free volume. There are other arguments against the ideas of iso-free volume. Thus, Kastner[42] observed that the dielectric losses decrease during isothermal decrease in volume, which shows that relaxation time depends on the free volume. However, the reduction factor calculated assuming that the relaxation time is determined solely by the free volume differs significantly from that found experimentally.

Serious objections against the concept of iso-free volume have been expressed[43] on the basis of published results[44]. It was shown that β-relaxation in poly(methyl methacrylate) and poly(hydroxypropylene glycol) under constant pressure and constant volume conditions proceed analogously. This is difficult to reconcile with the concept assuming that the changes in viscosity and mean relaxation time are due mainly to a change in free volume. To keep this concept in force it is necessary to postulate the existence of a large negative expansion coefficient for the occupied volume.

A departure from the Simha–Boyer equation for linear polymers with increase in the length of the side-radical was observed by Simha[45]. Mandelkern and coworkers[36] used many published results and their own experiments to try to find the limits of applicability of the Simha–Boyer equation. $\Delta\alpha \cdot T_g$ and $\Delta\beta \cdot T_g$ were plotted against T_g, where

$$1/v\,[(\partial v/\partial T)_l - (\partial v/\partial T)_g] \equiv \Delta\alpha$$

and

$$[(\partial v/\partial T)_l - (\partial v/\partial T)_g] \equiv \Delta\beta.$$

It was found that $\Delta\alpha \cdot T_g$ and $\Delta\beta \cdot T_g$ are not constant and consequently the Simha–Boyer equation is of restricted application. The results obtained show that $\Delta\alpha \cdot T_g$ increases with T_g therefore it is incorrect to use concepts including the product $\Delta\alpha \cdot T_g$ as a universal constant in theoretical investigations of glass formation. Mandelkern and coworkers[36] emphasise that this conclusion does not touch the free volume theory itself or its role in glass formation phenomena.

Practical arguments in support of the concept of iso-free volume and attempts at the direct determination of f_g from experimental results have not been given. Thus whereas Curro[46] found $f_g = 0.0261$ for poly(methyl methacrylate) on the basis of a determination of free volume from results on the difference in the specific volume of a polymer and its partial volume in solution, Buniyat-Zade and Ismailov's studies[47] of the temperature dependence of specific volume gave $f_g = 0.025$ for linear polyethylene, whereas for branch-chain or with graft acrylonitrile chains the f_g considerably exceeds the universal value, reaching 0.127. In considering the state equation of the polymers and the characteristics of the vitreous state, Curro[46] found that the agreement between the experimental results and the product $\Delta\alpha \cdot T_g$ is only semiquantitative. It was also shown[48] that the relation between T_g and pressure, which is predicted by the iso-free volume concept, is not observed by many polymers which also casts doubt upon it. Letunovskii and Zelenev[49] calculated the free volume fraction by starting from the relation they proposed:

$$T_\infty = T_g - f_g/(\alpha_l - \alpha_g),$$

where T_∞ is the temperature at which the viscosity tends to infinity. Assuming that there is a better basis for this equation, since it does not contain the arbitrary quantity B of the Williams–Landell–Ferry equation, Letunovskii and Zelenev[49] found $f_g = 0.0048$ for poly(methyl methacrylate) which is significantly lower than the universal value. The lower free volume fraction at T_g for n-alkanes and polyethylene than for vinyl polymers has been found[1,50].

A very interesting approach to the theoretical prediction of the limiting value of $\Delta\alpha \cdot T_g$ has been published[35]. Free volume theory has been used to consider the thermodynamics of the mixing of molecules with holes. As a result Sanchez[35] concluded that

$$T\alpha_h = \frac{E_h/RT}{\exp(1 - 1/r + E_h/RT) - 1}, \tag{12}$$

where α_h is the fraction of thermal expansion associated with the change in the concentration of the holes (expansion of the free volume), E_h the hole formation energy,

$$r = M/\rho v_h N_A,$$

N_A is Avogadro's number, M the molecular mass, ρ the density of a hole-free liquid at absolute zero, and v_h the hole volume. The $1/r$ term is very small for polymer systems and then $T\alpha_h$ is a function only of E_h/RT. The quantity α_h is identified with the experimentally determinable change in the coefficient of thermal expansion at T_g, that is:

$$T_g\alpha_h = T_g \cdot \Delta\alpha.$$

The graph constructed from Eqn. (12) shows that the predicted value of $\Delta\alpha \cdot T_g$ passes through a maximum at a value of 0.159, which corresponds to $E_h/RT = 0.841$. Almost all the values of $\Delta\alpha \cdot T_g$ given in the literature lie below this theoretical limit. The hypothetical value of $\Delta\alpha \cdot T_g$ varies relatively little with hole formation energy. For E_h/RT between 0.5 and 2.0 we have $0.105 < \Delta\alpha \cdot T_g < 0.159$.

It has been shown[35] that changes in the difference between the expansion coefficients at T_g can be predicted from the constant of the Williams–Landell–Ferry equation ($T_\infty = T_g - C_2$). Then

$$\Delta\alpha = 2(T_\infty/T_g)[\exp(1 + 2T_\infty/T_g) - 1]^{-1}.$$

Here it is assumed that $T_\infty = T_2$, where T_2 is the temperature of a second-order transformation, according to the Gibbs–DiMarzio theory[40]. The free volume is then determined as:

$$v_f = (v - v_\infty)/v_0,$$

where v_∞ is the macroscopic volume of the liquid at the temperature T_∞ and v_0 is the volume of the molecules.

Theory predicts that at the T_0 appearing in the Fogel equation the iso-free volume state should occur. However, consideration of the calculated values of f_g shows that this does not take place. Other examples of departures from the behaviour predictable within the framework of the iso-free volume concept have been described[51,52]. We have already noted Kanig's conclusion about the variation of f_g with the flexibility of the polymeric chain[31] and our conclusion about dependence upon the packing density[32,33]. In this connection it is desirable to consider the problem of whether there really exists a definite relation between the free volume fraction at the glass formation temperature and the molecular parameters of the polymeric chain.

V. VARIATION OF THE FREE VOLUME FRACTION AT THE GLASS FORMATION TEMPERATURE WITH THE MOLECULAR PARAMETERS OF LINEAR POLYMERS

As noted above, the constancy of f_g for various polymers differing in their chemical structure is only a rough approximation. From several qualitative arguments and results on glass formation in a series of polyurethanes it was suggested[53] that the experimentally observable change in free volume for different polymers can be connected with their molecular parameters, above all with the flexibility of the chain. It is now desirable to prove this in detail by finding the relation between the free volume and the nature of the molecular packing.

For this purpose it is convenient to use the definition of the free volume fraction given by Litt and Tobolsky[19], that is, to state, in accordance with Fig. 1, that the occupied volume is v_3''. From an analysis of results on the molecular parameters of a series of polymers there is a definite tendency towards an increase in the ratio v_3''/v_g as the size of the side-groups of the polymeric chain is increased. The ratio of the volumes of the polymer in crystalline v_c and amorphous v_a states is connected with the characteristic parameter of the chain a/σ, where a is the thickness of the chain determined by the dimensions of the elementary cell and σ a steric factor or the flexibility parameter of the isolated polymeric chain, which usually can be estimated from measurements of the characteristic viscosity in the ideal solvent[54]. A relation was found between v_c/v_a and a/σ.[55,56] It was found that there is a definite tendency for v_3''/v_g to increase with a/σ.

It can be proved that the ratio v_3''/v_g equals the ratio of the packing factors of the polymer in the amorphous and crystalline states K_a/K_c at T_g, since by definition

$$K_a = N_A v_i/v_a \quad \text{and} \quad K_c = N_A v_i/v_c;$$

here v_i is the van der Waals' volume of the repeating unit of the chain, and N_A Avogadro's number. We note that the calculated values of $(K_c)_g$ correlate with the characteristic parameter of the chain a/σ, and the ratio between them can be expressed as follows:

$$(K_c)_g = 0.9(1 - 0.058\, a/\sigma). \tag{13}$$

Hence we can state that the free volume fraction at the glass transformation temperature, as determined according to Eqn. (2) will be less when the packing of the chains in the bulk of the polymer becomes looser. This conclusion agrees with the analogous quantitative conclusion reached earlier[35,34].

Presumably this conclusion is general for all polymers in the amorphous state. However, Eqn. (13) cannot be applied directly to polymers which do not crystallise, since then v_3'' or a is unknown. In trying to extend to these polymers the ideas expressed above we can propose another definition of f_g, analogous to the Simha–Boyer expression:

$$f_g=(\alpha_l-\alpha_g)(T_g-T''),$$

where T'' is a comparison temperature connected with the occupied volumes v_0'', v_3'', and v_2'', as is shown in Fig. 1. For example, $T''=0$ K corresponds to the Simha–Boyer theory, $T''=T_3$ to the Little–Tobol'skii theory, and $T''=T_2$ corresponds to the Williams–Landell–Ferry definition. We obtained[53] the following empirical equation, connecting T_g with the chain rigidity parameter σ:

$$T_g=A(\sigma-b), \tag{13a}$$

in which A and b are constants. This equation can be compared with the Simha–Boyer equation (7). If now it is assumed that A is proportional to K_1, Eqn. (7), and $\Delta\alpha$ is proportional to $(\sigma-b)^{-1}$ and then Eqns. (7) and (13a) are solved for T_g, we obtain:

$$\Delta\alpha, \mathrm{K}^{-1}=4.2\cdot10^{-4}(\sigma-1)^{-1}. \tag{14}$$

As was shown above, our results[53] are a basis for this assumption. Consequently, if the assumed proportionality between the parameters of the equations is real, the constant K_1 in Eqn. (13) does not have to be the same for all the polymers.

Clearly $\Delta\alpha$ is actually not constant but increases with the flexibility of the chain (that is, with decrease in σ). Hence if the Simha–Boyer equation and our Eqn. (13) are valid, the relation between $\Delta\alpha$ and $\Delta\alpha\sigma$ should be straight lines with slope unity. And actually $\Delta\alpha$ has a tendency to increase as σ is reduced, although this behaviour also cannot be described quantitatively by Eqn. (14). The departure of the experimental points from the theoretical line becomes especially significant when $\Delta\alpha$ is reduced.

It is noted that the best agreement between the experimental values of $\Delta\alpha$ and the theoretical relation is observed for those polymers which obey the Simha–Boyer rule. This again emphasises that f_g is not constant. A more complete representation of the relation between $\Delta\alpha$ and σ is given by the relation between $\lg\Delta\alpha$ and $\Delta\alpha\sigma$, for which considerably better agreement is observed between the experimental points and the theoretical straight line even for those polymers which do not obey the Simha–Boyer rule.

It seems possible to give a qualitative explanation of the observed relation between $\Delta\alpha$ and the rigidity parameter σ. By definition, α_g depends on the anharmonicity of the thermal vibrations of the individual molecules or of the groups they contain and hence the physical nature of α_g is approximately the same for polymers and low-molecular weight liquids. On the other hand, the nature of α_l is not the same. The value of α_l for liquids is reduced as the forces of intermolecular interaction are increased, whereas T_g increases[16], and therefore it is natural to expect an approximately constant product $\Delta\alpha\cdot T_g$, that is, the Simha–Boyer rule is satisfied.

For polymers the quantity α_l does not depend solely on the intermolecular interaction, which affects the mean distance between the centres of gravity of the molecular groups of the chain, but also on the ability of the macromolecules to undergo conformational transformations, which are closely connected with the flexibility of the chain. Then for polymers we can write approximately

$$\Delta\alpha=(\alpha_l)_p-\alpha_g=(\alpha_l-\alpha_c)_m+\Delta\alpha_{\mathrm{conf}},$$

where the indices m and p refer to the polymer and monomer, $\Delta\alpha_{\mathrm{conf}}$ is the additional contribution to $(\alpha_l)_p$ due to the change in the number of conformations of the chains in the melt[56]. Hence it seems that the numerical value of the coefficient $\Delta\alpha$ for the polymers will depend significantly on the size of the "polymer" contribution $\Delta\alpha_{\mathrm{conf}}$, which apparently will be different for polymers with chains of different flexibility.

The conclusion that the free volume fraction at T_g is not a universal constant for linear polymers of different molecular structure can be confirmed qualitatively by the following arguments[57]. We assume that at temperature much lower than T_g the polymeric chains are in a state with minimal energy of the intermolecular interactions, that is, the fraction of the bonds with high energy equals zero[40]. On the other hand, the equilibrium of the fraction of bent chains at $T>T_g$ obey Boltzmann statistics. Then the fraction of bent chains at T_g can be determined from the well-known relation:

$$\varphi_g=[\exp(-\varepsilon/kT_g)]/[1+\exp(-\varepsilon/kT_g)]. \tag{15}$$

From Eqn. (15), the fraction φ_g decreases with increase in ϵ/kT. On taking into account the fact that an increment of volume for a single bent bond will be greater than for a straight bond, this indicates that the fraction of the free volume f_g at T_g which can be identified with the quantity φ_g of Eqn. (15) will actually decrease as the packing density of the polymers in the crystalline state is reduced. Treatment of the experimental results on the variation of the glass formation temperature with the flexibility of the polymeric chain[57] showed that by starting from general equation (13) an expression can be obtained for linear polymers relating T_g with the free volume in the following manner:

$$T_g=T_g(\mathrm{LPE})+[\sigma-\sigma(\mathrm{LPE})]\cdot Y(f_g),$$

where σ(LPE) refers to linear polyethylene, and $Y(f_g)$ is a function which can be determined from the experimental results.

Hence the results considered show the need for reconsidering the concept of glass formation temperatures as corresponding to the state of iso-free volume. It is remarkable that f_g decreases as a/σ is increased. These changes are brought about mainly by variations in the packing coefficients in the crystalline state, whereas the packing coefficients in the amorphous state $(K_a)_g$ remain almost constant. It seems reasonable to assume that this quantity $(K_a)_g$ should be chosen as a measure of the free volume at glass formation temperature. In other words, the determination of the occupied volume as a characteristic volume or van der Waals' volume of a repeating unit of a chain with a low (approximating to zero) thermal expansion coefficient is the most suitable. Such an approach does not conflict with the possible definition of free volume discussed by Bondi[58].

VI. THE CONCEPT OF FREE VOLUME DISTRIBUTION

From the standpoint of the ideas introduced that the free volume fraction at T_g is not constant even for the same type of molecular movements in different polymers and for different types should be different, a consideration of the distribution of the free volume in a system is of interest.

The concept of free volume distribution was developed by Turnbull and Cohen[16]. It is based on the assumption that molecular movements, like transport phenomena, take place only when the vacancies or holes in a body have dimensions greater than some critical value v^*. This critical volume arises as a result of the redistribution of free volume in the system. It is assumed that such a redistribution of free volume takes place without consumption of energy. The concept of excess volume is therefore introduced:

$$\bar{v} - v_0 = \overline{\Delta v}$$

(where $\bar{v}$ is the specific volume and v_0 the volume of the molecules) and the free volume is v_f, such that

$$\overline{\Delta v} = v_f + \Delta v_c,$$

where Δv_c is the volume determined by the thermal vibrations.

It was suggested[16] that only part of the excess volume v_f can be redistributed without consumption of energy. This takes place above the critical temperature T_2. In this instance the thermal expansion of the amorphous phase at low temperatures is due solely to the anharmonicity of the thermal vibrations of the molecules. Hence $v_f \simeq 0$ at the $T < T_2$ and $\Delta\bar{v} \simeq \Delta v_c$. It is also suggested that in this instance an increase in entropy due to the change in volume is also very small. As the temperature is raised and a certain value of Δv is reached the main contribution starts to be the expansion of the "free" for redistribution volume,

$$v_f = \alpha\bar{v}_m(T - T_2),$$

where α is the mean expansion coefficient, and $\bar{v}_m$ the mean volume of the molecules in the temperature range from T_2 to T_g.

The free energy of the amorphous phase should be a minimum when the free volume is distributed in a random manner. Since a random distribution of the volume occurs only in the amorphous, and not the crystalline, phase, under the condition $\Delta\bar{v} > \Delta\bar{v}_g$ the amorphous phase should be more stable than the crystalline, owing to the positive configuration entropy, determined by the definite distribution of the free volume. Therefore, according to Turnbull and Cohen[16], the glass formation temperature of the amorphous phase is defined as the temperature at which the excess volume reaches the value $\Delta\bar{v}_g$, above which a free volume exists.

The probability that the free volume at a given temperature exceeds some value v^* is, according to Fujita[6], given by the relation

$$P(v^*) = \exp[-Bv^* | \langle v \rangle],$$

where $\langle v \rangle$ is the mean free volume of one molecule, that is, the total free volume divided by the number of molecules; B is a numerical factor close to unity. Another definition can also be introduced—the mean free volume per unit volume, that is, the mean free volume fraction f. On putting $Bv^* = C$, then

$$P(C) = \exp(-C/f).$$

These ideas were used to describe diffusion in polymers of low-molecular-weight substances[59]. The mobility of the molecules m_d in the medium will depend on the probability that the molecule will appear in a neighbouring hole is large enough to ensure its displacement. We will use C_d to denote the value of C corresponding to the least hole size necessary for such a displacement. Then

$$m_d = A_d \exp(-C_d/f),$$

where A_d is a factor depending upon the size and form of the solvent molecules.

Litt[60] developed ideas about the least possible diameter b^* of a hole associated with a macromolecule for effecting molecular or segmental motion. According to him, only a hole with a diameter not less than b^* can affect the viscosity. Hence a modified Doolittle equation can be obtained:

$$\ln(\eta/\eta_0) = \pi^{1/2}/[A(T^*/T)^{3/2}(1 + T^*/T)^{-1}\exp(T^*/T)],$$

where

$$A = {}^4/_3\,\pi b^* n,$$

n is the number of molecules per 1 cm^3, $T^* = 4\pi b^{*2}\epsilon/k$, ϵ is the surface tension, k the Boltzmann constant, and T^* the characteristic temperature. The A varies from 0.75 for flexible to 1.4 for rigid polymers. The constant $T_g/T^* = 0.360 \pm 0.1$ was observed for many systems. It is suggested that such a modification of the free volume theory improves its physical reliability. Thus, whereas according to the Williams–Landell–Ferry equation $f \simeq 0$ at $T_g = 50°C$, and then $\ln\eta \rightarrow \infty$, in the example under consideration f/f decreases monotonically at $T < T_g$ reaching zero only at 0 K.

The need to divide free volume into its constituent components was also stated by Razumovskaya and Bartenev[61]. It was noted that the free volume fraction according to Williams–Landell–Ferry is less than its estimate from other results, for example, from compressibility. According to Razumovskaya and Bartenev's results[61], for several polymers the free volume fraction at the glass formation temperature reaches 10–15%, whether it is calculated from compressibility results or from assumptions concerning the additivity of volume for different atomic groups. Mason[62] explains this difference by certain "holes" having lost their characteristic mobility, termed "frozen". Reference is made here not to a quantitative retardation of the hole migration process, but to the complete exclusion of some of the holes from the process. Hence a distinction must be made between the geometric free volume (~10–15% of the entire volume), which corresponds to the Simha–Boyer definition, and the physical free volume, determined by the relaxation time (3%).

The physical free volume v_f is defined as $v_f = v_d n^*$, where v_d is the volume of excited holes, n^* the number of excited holes. The fraction of excited holes at the glass formation temperature will then be $n^*/n = f^*/f_{eff} \simeq 0.1$, where n is the total number of holes in the system, f^* the fraction of physical free volume, and f_{eff} the fraction of geometric free volume. Glass formation is regarded from this standpoint as "freezing" of the characteristic frequencies, which is accompanied by a decrease in the free volume and mobility of the holes. In this it is suggested that molecular rearrangements are brought about by the movement of holes corresponding to definite kinetic units with a characteristic frequency of the thermal vibrations. Such a position corresponds to the ideas we have developed that the motion of parts of different size or different groups of atoms requires a different free volume.

Actually, results on the isothermal contraction for several polymers[3] treated on the basis of the free volume theory show that the quantitative kinetics are not described by a simplified model of the polymer with a single mean relaxation time. Many investigations showed that instead of one relaxation process, relaxation spectra and a distribution of relaxation times must be considered. Kastner[59] attempted to connect this distribution with the free volume distribution. In this connection, Covacs concluded[3] that in considering only the mean parameters of macroscopic specimens (complex modulus, volume, heat content, etc.) the free volume concept should be linked with the change in the molecular mobility and with different types of molecular movements. These processes include a wide distribution of delay times, which can be associated with the local distribution of holes.

Mason[62] developed ideas about the distribution of free volume to explain the diffuseness of the change from the vitreous state to the liquid by assuming the localisation of part of the free volume, which distinguishes the polymeric substance from the true liquid state, where the free volume is not localised. In connection with rubber vulcanisers Mason assumes that in the non-cross-linked state there can still be an arbitrary distribution of the free volume v_f connected with the free volume v_f' of each monomeric unit. Taking the universal value of 0.025 for f_g in this, he assumes that the mean volume per monomeric unit is expressed as

$$\bar{v}' = M_v/nN_A,$$

where M is the molecular mass of the rubber, n the number of monomeric units in the molecule, and v the specific volume. The monomeric specific free volume f' will be defined as

$$f' = v_f'/\bar{v}' = (nN_A/M_v)v_f'.$$

The geometry of the packing can be characterised by distribution functions $P(f')$ which represent the density of the monomeric units with the specific free volume[62].

The effective T_g for a monomeric unit is determined by the condition $f' = f_g$. Hence the number of monomeric units in 1 g rubber at temperature T_g equals

$$n_g = \int\limits_0^{f_g} P\mathrm{d}f'$$

in the vitreous state and

$$n_l = \int\limits_{f_g}^{\infty} P\mathrm{d}f'$$

in the liquid state; under normalisation conditions

$$\int\limits_0^{\infty} P\mathrm{d}f' = N_A n/M.$$

Hence the distribution coefficient is

$$\alpha = \left(\int\limits_0^{f_g} P\mathrm{d}f'\cdot\alpha_g + \int\limits_{f_g}^{\infty} P\mathrm{d}f'\cdot\alpha_l\right)\Big/\int\limits_0^{\infty} P\mathrm{d}f'$$

and

$$\alpha - \alpha_g = \frac{M(\alpha_l - \alpha_g)}{N_A n}\int\limits_{f_g}^{\infty} P\mathrm{d}f'.$$

In the last equation it is assumed that at an arbitrary temperature T there are units present in both the vitreous and in the liquid state, as determined by the distribution coefficient. The coefficient α is regarded here as the sum of the expansion coefficients of each region with allowance for the numerical fraction of the units.

The value of the integral, representing the number of monomeric units found in the liquid state decreases from $N_A n/M$ at a temperature above T_g (where $\alpha = \alpha_l$) to zero below T_g (where $\alpha = \alpha_g$). When all the monomeric units have the same specific free volume f', then the change into the liquid state will take place at a single temperature. The "blurring" of the change for some interval of T is connected with the distribution of f' and the temperature interval in which α decreases from α_l to α_g gives a measure of the width of this distribution. Hence assuming a normal distribution of f' at a temperature above T_g the mean value of f' will equal the macroscopic f, and the distribution will be:

$$P = P(f) = \frac{1}{\sigma\sqrt{2}}\exp\{-[(f' - f)^2/2\sigma^2]\},$$

where σ is the dispersion. Hence with allowance for the normalisation conditions, we have:

$$\alpha - \alpha_g = \frac{M(\alpha_l - \alpha_g)}{N_A n}\,\frac{1}{\sigma\sqrt{2}}\int\limits_{f_g}^{\infty}\exp[-(f' - f)^2/2\sigma^2]\,\mathrm{d}f'.$$

Close to T_g the value of σ can be taken as constant, and then the temperature enters into the function being integrated only through f. Bearing in mind the equations obtained, Mason[62] succeeded in calculating the distribution of the free volumes for monomeric units $P(v_f')$ with vulcanisers which are characterised by a different cross-linking density.

Ideas about the free volume distribution provide a significant contribution to understanding the mechanism of the glass formation processes in polymers and in the development of free volume theory. The need for taking into account the free volume distribution in the system was also shown in passing by Kanig[31] and Sanchez[35]. However, ten years elapsed before a new treatment of the problem of free volume distribution based on the ideas of the distribution of holes according to size appeared. Kilian[63] analysed glass formation from the viewpoint of thermodynamics as the displacement of the polymeric chains with holes of homogeneous dimension, the mixture being regarded as a saturated solution of linear chains, containing y_p repeating units. However, since the vacancies or holes exhibit a distribution in sizes, a quasistatistical glass formation temperature is considered at which glass formation takes place according to a cooperative mechanism. From this we calculated the partial molar enthalpy of mixing with allowance for the zero interaction of the holes with one another and of the holes with the polymer. It is assumed that the formation of holes in the medium always requires the same excess enthalpy. On this basis Manabe and Takayanagi[64] obtained the following equation for T_g:

$$\frac{1}{T_g} = \frac{R}{A_p^h\varphi_p}\cdot\frac{1}{y_p} + \frac{A_p^s}{A_p^h} + \frac{R}{A_p^h y_{Li}\varphi_p^2}\left\{\frac{y - \varphi_p}{\bar{y}_i}\,y_{Li} - \ln\varphi_{Li} - 1\right\},$$

$(i = 1, \ldots, N)$,
where A_p^h is the specific entropy of formation of any holes, A_p^s the excess entropy of formation of the holes, $\varphi_p = y_m n_m/\Sigma y_i n_i$, y_{Li} is the hole size, $\bar{y}_i$ the mean particle size in the mixture, φ_{Li} the fraction of holes of size i. From this equation, it follows that for a polymeric system in which there is a distribution of holes according to sizes,

the volume fraction of holes φ_{Li} should be different and depend on y_{Li}. From the thermodynamic point of view, for each fraction of holes there is a quantity y_{Li}, which should satisfy the condition of thermodynamic equilibrium.

Comparison of the last equation with published results relating T_g with the chain length y_p showed[63] that if the normalisation condition is taken to be

$$\Sigma \varphi_{Li} = 1 - \varphi_p,$$

then

$$\varphi_{Li} = \left[\frac{(1-\varphi_p)\, e}{(1-\varphi_p)\, e + 1} \right]^{y_{Li}} \cdot \frac{1}{e}$$

is a distribution function for the holes according to size. When the iso-free volume condition $\varphi_L(T_{g\infty}) = \text{const}$ is obeyed, the distribution function φ_{Li} is also invariant with respect to the system.

Calculations of the entropy of formation of the holes showed that it is negative, that is, there cannot be a statistically disordered homogeneous distribution of holes. However, Kilian[63] considers as problematical the distribution of holes according to the condition $1 \leqslant y_{Li} = \infty$ without a connection with the molecular structure. The distribution function is monotonic for a saturated mixture and the volume fraction of holes of large dimension rapidly decreases as y_{Li} is increased. It is assumed that the ideas about distribution correspond best to the statistical nature of the molecular configurations in the liquid phase. According to Frenkel', the free volume in a liquid in principle is not connected with the sizes of the molecules but is comparable with the atomic dimensions[29]. It must be taken into account that the holes should be distributed irregularly, at least in a polymer to ensure that a variety of types of molecular movement is possible.

The concept of free volume distribution was developed further by Manabe and Takayanagi[64-66], who applied it to the glass formation temperatures of mixtures of two polymers. Comparison of the theoretical ideas with experiment showed that a different distribution of the free volume is possible in mixtures. They found experimental proof that the glass formation temperature corresponds to the iso-free volume state. The same T_g can also correspond to different distribution functions owing to a difference in the structure of mixtures. Hence although the free volume is an important characteristic of the glass formation process, different distribution functions of T_g correspond to different distribution functions of free volume.

The inapplicability of the concept of iso-free volume to mixtures of polymers was also shown in studies[68, 69] based on theoretical ideas about the distribution and localisation of the free volume in heterogeneous polymeric systems.

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The results of the many investigations reviewed in the present paper suggest that the concept of glass formation as a state of iso-free volume cannot be regarded as justified, either theoretically or experimentally. This became especially clear after it was observed that even for the same polymer the free volume fraction could change depending upon the conditions of formation of its structure[68]. All this shows that although the concept of free volume is physically reasonable, its use to describe the properties of polymers involves considerable difficulties in some instances. This restriction is evident particularly clearly in considering glass formation as a process corresponding to the iso-free volume condition.

Therefore one of the main tasks in the field of free volume theory and the theory of glass formation is the development of new concepts and the production of new parameters of corresponding states. Thus, Miller[23] introduces the concept that glass formation corresponds to an iso-relaxation state, and at molecular masses below critical it corresponds already to the condition of an "iso-viscous" state. We assume that since the free volume concept itself characterises the state of ordering of the system (especially when we consider the free volume distribution function), then the thermodynamic description of the processes which take place during glass formation through configuration entropy and the breakdown of the kinetic description of this process is more hypothetical. According to Adam and Gibbs[1], glass formation takes place when the system reaches some minimum configuration entropy. Its value can be calculated from the relation:

$$\Delta S_c = \Delta C_p \ln (T_g/T_0),$$

where ΔC_p is the jump in heat capacity during glass formation. Such an approach shows, in particular, that the quantity ΔS_c can also reflect the effects connected with the existence and distribution of free volume. Hence ideas about glass formation as an isentropic transformation, in accordance with the Gibbs–DiMarzio theory, can be extremely promising.

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Industrial Applications of Amino-acids

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Aspects of the use of amino-acids in various branches of industry—as food additives and surface-active agents, in the production of polymeric materials, in electrochemical manufacture, etc.—are surveyed on the basis of works of reference and the patent literature up to 1975. A list of 273 references is included.

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I. INTRODUCTION

During recent years the manufacture of amino-acids has been actively developed throughout the world (Table). Their chief consumers, ensuring a steady demand, have been the food industry, in which sodium glutamate is used as a flavour intensifier, and lysine as an additive to increase the nutritional value of bread, animal husbandry, and poultry farming, where lysine, tryptophan, threonine, and methionine are used to increase the food value of protein feeds.

World production of amino-acids (1974).

Product	Annual production, tonnes	Method*
Sodium *L*-glutamate monohydrate	200 000	M, X
L-Methionine	50 000	X
L-Lysine monohydrochloride	20 000	M
L-Tryptophan	20	X
L-Threonine	20	X
Glycine	2 000	X

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*M = microbiological; X = chemical.

The present review does not cover such well known fields of application as animal husbandry, parenteral feeding, etc., on which a vast review literature exists. Special attention is paid to less well known trends—the possible use of amino-acids in pharmacology and cosmetics, as food additives and surface-active agents, in the synthesis of polymeric materials, as pesticides, in the electrochemical industry, etc. Several fields of application have not been developed because of the very high cost of amino-acids, due mainly to the low volume of production. The recognition of new consumers will help to increase production and thereby ensure the comprehensive application of amino-acids.

II. THE FOOD INDUSTRY

The chief consumer of amino-acids at the present time is the food industry. Problems of the enrichment of food products with indispensable amino-acids and of balancing the diet (i.e. adding the missing amino-acids to low-quality proteins) have been widely discussed in the Soviet[1-3] and foreign[4-8] literature, so that we will not dwell on them. Food products can be enriched with lysine, threonine (rice, wheat, sorghum, etc.), tryptophan (maize, wheat). and methionine (soya-bean and peanut flour). However, the balancing of cereal products with pure amino-acids (other than lysine) has not yet found widespread application in the food industry[3], although it improves the nutritional properties of vegetable protein. *L*-Threonine and *L*-tryptophan have not yet found practical application for product enrichment, yet vigorous research has been undertaken on the possible use of these important saturated amino-acids, which is prevented by their high price. Among possible fields of application of these and other amino-acids are babyfoods[1], enrichment of low-calorie food[1,6,9-11], dietetic feeding[12-15], and special diets for cosmonauts[16].

While possessing extremely interesting and diverse properties, amino-acids have come to find application in the food industry, as microbiological and chemical methods for obtaining them have developed, mainly as seasonings, to confer taste and aroma on food products, and as antioxidants.

The main requirement to be met by various kinds of food additives is that they should not be toxic. In the opinion of many experts amino-acids, being together with proteins natural constituents of food products, fully satisfy this requirement. Many publications have appeared, including Refs. 17–19, on the determination of the degree of toxicity of amino-acids.

Glutamic acid has become the most widely used in the food industry: salt sodium glutamate is commonly employed as an effective taste intensifier. It is widely used to improve the taste of meat and vegetable dishes[20], as a mixture with table salt, and for modifying the taste of synthetic sweetening agents[21]; in many countries it is added to all products during canning, freezing, or prolonged storage[3,20]. The patent literature suggests that the boundaries of its application continue to be extended[22-28]; in Japan its production has formed the starting point for industrial methods of obtaining amino-acids, and has stimulated vigorous research on the application of other amino-acids in this way.

In fact many amino-acids possess their own unique flavour and are important elements in the taste of food products. These properties of individual amino-acids have been studied by many investigators and in especial detail by groups under the leadership of Yoshida[29] and of Solms[30,31]. The usual pure amino-acids were found to be respectively tasteless or with a barely perceptible taste (*D*-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 (in order of diminishing sweetness—*D*-tryptophan, *D*-histidine, *D*-phenylalanine, *D*-tyrosine, *D*-leucine, *L*-alanine, and glycine), bitter (in order of diminishing bitterness—*L*-tryptophan, *L*-phenylalanine, *L*-tyrosine, and *L*-leucine), and "sulphurous" (*D*- and *L*-cysteine and *D*- and *L*-methionine); *D*-isomers of bitter amino-acids are usually sweet. *L*-Aspartic and *L*-glutamic acids exhibit a sour taste, but when neutralised their solutions have a pleasant flavour; their *D*-isomers are tasteless. These results confirm the relation between the taste and the configuration of amino-acids. The taste is assumed to be due to "three-point" stereospecific adsorption on taste receptors in the surface of the tongue[7].

The majority of methyl, ethyl, benzyl, and t-butyl esters of α-amino-acids have a bitter taste or are tasteless. However, the hydrochloride of the t-butyl ester of *L*-alanine possesses an intensely sweet taste: a given weight is equivalent in sweetness to ~75 times that weight of sucrose[32].

The taste of a product is determined not only by the amino-acids but also by its content of mononucleotides (such as inosinic and guanylic acids), organic acids, sucrose, and inorganic acids. Peptides and metabolites of amino-acids (such as betaine and creatine) promote complexity, the "bouquet" of flavour sensations. A great contribution to the taste of plant products is made by glutamic acid, and also by other amino-acids, organic acids, and sucrose. Free amino-acids present in certain foodstuffs may completely determine the taste; in other products amino-acids or their mixtures either strengthen the taste or supply body to it[7,33,34]. The buffering properties of amino-acids also influence flavour[34]. A required taste sensation can be matached by combining various chemical substances, including amino-acids. At the present time amino-acids can be used to strengthen and improve the flavour characteristics of many food products. However, only monosodium glutamate and glycine have found practical application for these purposes.

Glycine is a typical example of sweet amino-acids, exhibiting a "refreshing" sweetness equivalent in intensity to that of sucrose. At the present time it is widely used in the Japanese food industry for the manufacture of seasonings, non-alcoholic drinks, soups, marinades, various fish products, and delicatessen (0.1–1% in amount depending on the type of product)[7,35–38]. It not only serves as sweetening agent but also creates the foundation of a taste or improves the flavour, by mitigating bitterness and saltiness. It is used also for the modification of artificial products to remove an unpleasant aftertaste.

Amino-acids and mononucleotides act synergistically with respect to taste: the effect of the flavouring agent sodium inosinate is strengthened by the addition of sodium monoglutamate. The synergistic effect of mononucleotides is evident also in combination with sodium *L*-aspartate, *L*-asparagine, and glycine, which is used in recipes for seasonings to improve the taste of foodstuffs and drinks[36,39–41].

Patent information has appeared on such taste-improving agents as *L*-lysine palmitate[42] and glutamylglycylserine[43]. A wide search is being made for new sweetening agents, especially those of peptide character. The taste of peptides is independent of the type of component amino-acids, being determined by the overall structure of the peptide. Dipeptides formed by sweet amino-acids are generally tasteless, whereas peptides containing residues of bitter amino-acids all, without exception, have a bitter taste. In 1969 the discovery was reported[44] of the methyl ester of *L*-aspartyl-*L*-phenylalanine, possessing a sweet taste (sweeter than sucrose by a factor of 150). Investigations on the dependence of taste on structure have shown that a dipeptide must contain aspartic acid to be sweet. Many sweetening agents have since been patented, representing various modifications of this dipeptide[14,45,46]; they can be used for dietary products (e.g. for diabetics). The methyl esters of *L*-aspartyl-*O*-t-butyl-*L*-serine and *L*-aspartyl-*O*-t-pentyl-*L*-serine are sweeter than sucrose by factors of 130–200, and similar to the latter in the character of the sweet taste, have no odour or unpleasant aftertaste, and can be used to improve the flavour of chocolate, confectionery, tea, farinaceous products, fruit juices, etc.[47,48] Much information has been published on the possible application as sweetening agents of both peptide and non-peptide derivatives of aspartic acid[12,14,44–53]. Either *D*- or *DL*-tryptophan can be used as synergist, intensifying the sweetness of saccharin and eliminating its inherent unpleasant aftertaste[45,53,54].

One of the chief reactions producing aroma in almost all food products is Maillard's, consisting in the interaction of the amino-groups of peptides, amino-acids, and proteins with the glycosidic hydroxyl of sugars. This reaction is especially important when the aroma results from heating the food, e.g. bread or meat[55]. According to Tressl[56] several hundred aromatic compounds, many formed by reactions between amino-acids and reducing sugars, have been identified in the aroma of products that have been subjected to heat. Thus, although most individual amino-acids are odourless, when heated with other compounds they yield odours that are specific to the given type of amino-acid. Herz and Shallenberger[57] studied the aroma produced when certain amino-acids were heated with glucose at 100 and 180°C for 1 h, and found that glycine, proline, methionine, valine, and arginine yielded the odours respectively of caramel, bread, potatoes, chocolate, and burnt sugar.

As early as the 1960s it was noted that the Maillard reaction offered great prospects of "synthesising" food odours[20], and attention has now been paid to its utilisation. Since the decisive role of the reaction is indicated by the appearance of the aroma of bread from valine, leucine, proline, and lysine in model experiments, it is recommended that a mixture of these amino-acids or the products obtained by heating the mixture with saccharides should be added to improve the flavour and aroma of farinaceous confectionery, and proline mixed with dihydroxyacetone in bread manufacture[58,59]. Valine and phenylalanine have already been used in Japan to improve the aroma of rice pastry. *L*-Lysine is added to coffee (10–70 mg/100 ml) for the same purpose[60]. It has been proposed[61] to introduce amino-acids (arginine, leucine, valine, lysine, etc.) together with dihydroxyacetone into tobacco, on the view that during curing they react with the latter to form aldehydes, which confer agreeable properties on the smoke.

Lysine, ornithine, histidine, arginine, aspartic acid, alanine, valine, leucine, isoleucine, and proline can serve as active ingredients of various deodorants for food products[62-64]. The specific odour of rice that has been stored for a long time can be removed by adding *L*-cysteine, *L*-lysine, and *L*-histidine[65]. Thus the definite influence of amino-acids on taste and aroma has led various investigators to make repeated attempts to improve the organoleptic indices of food products.

For several years Miyake et al. studied the influence of basic amino-acids on the taste properties of meat products. They showed that the organoleptic characteristics (tenderness, taste, odour) were improved by treating raw meat with basic amino-acids, especially arginine[66]. Patents have appeared on the use of histidine, lysine, cystine, and arginine to improve the quality of meat and fish products[67,68]. In the manufacture of sausages from the meat of warm-blooded animals or fish the fat distribution and the gelatinisation of the products are improved by the addition of 0.1−1% of a *D*-amino-acid (alanine, arginine, cysteine, etc.)[69].

Individual amino-acids and their mixtures can be introduced into compositions simulating the taste and odour of natural foodstuffs. Cysteine and cystine are important constituents in the creation of “meaty” odours, and are introduced into compositions possessing the taste of meat[7,20,27,70]. Monosodium *L*-glutamate must also be present to produce a fully “meaty” odour and flavour[26,27,70,71]. For example, a mixture of a hexose and a pentose is heated with cysteine or cystine in the presence of water to give compounds having the taste of meat. They are mixed in definite proportions with the hydrolysate of a vegetable protein, monosodium glutamate, sucrose, alanine, glycine, and a mixture of inosine and guanyl monophosphates. Heating the mixture alone and together with fats produces the flavours of soup and of gravy respectively[70]. Pentoses such as ribose and xylose are more active than are hexoses. Methionine is used to make a flavouring with the smell and taste of potatoes[72]. Such synthetic compositions will become especially timely in the future in connection with the production of artificial foods[26,27,70-74].

The development of the food industry has entailed an increasing demand for large quantities of antioxidants. The antioxidising properties of methionine have been known for a long time; it is widely used in edible oils and fats, in which a strong effect is apparent, with a favourable influence on the organoleptic indices of the product[75,76]. Progress has now been made in the use of other amino-acids for these purposes.

Soboleva and her coworkers[77] studied the antioxidant properties of several amino-acids in soft and hard margaine, vegetable oil, and butter. All the amino-acids used tended to inhibit oxidising processes in fats, but the efficiency of a particular amino-acid depended considerably on the type of fat. *DL*-Lysine, *DL*-tryptophan, and *DL*-methionine are effective antioxidants for the fatty base of soft and hard margarine; *L*-arginine hydrochloride, *DL*-tryptophan, *L*-cysteine, and *DL*-methionine for vegetable cooking fat; and *L*-arginine hydrochloride, *L*-asparagine, *DL*-norleucine, and especially methionine for butter. The introduction of synergists improves the antioxidant properties of amino-acids: mixtures with chemical antioxidants—butoxytoluene and butoxyanisole—are more effective than are the individual components.

Glycine is a good antioxidant for such emulsifiers as mono- and di-glycerides. Several amino-acids were studied in model experiments using methyl linoleate[78]. The best results were obtained with histidine and tryptophan, which can be added to powdered milk to preserve it from the most frequent defect of milk products—the “oxidised” aftertaste resulting from the autoxidation of milk fat[78,79]. Individual amino-acids, their derivatives, and various compositions with other compounds have been patented for use as antioxidants[38,80-83]. Lipids in food can be freed from rancidity by adding a salt of a basic amino-acid (such as lysine) and phytic acid[82]. Alkyl esters of aspartylphenylalanine $HOOC.CH_2.CH(NH_2).CO.NH.CH(CH_2C_6H_5).COOR$ (where $R = CH_3$, C_2H_5) are readily soluble in oils and fats, cause neither an unpleasant odour nor discoloration when heated, and can be used as antioxidants and emulsifiers for foodstuffs[83]. *N*-Acetylmethionine has a stronger antioxidant effect than methionine in cooking oil[84].

Many investigators have studied the antioxidant action of the coloured products formed by the Maillard reaction, first reported for melanoidins[85]. The coloured products formed from amino-acids and reducing sugars play an important part in stabilising fats against oxidation[86]. As a threose, dihydroxyacetone is more reactive towards amino-acids than are pentoses and hexoses, and therefore Ito et al.[87] have compared (in a model system) the antioxidant activity of the coloured products obtained with dihydroxyacetone, glucose, and xylose respectively. This shows strong variation with the sugar and with the amino-acid. The most active sugar (the threose dihydroxyacetone) gives products exerting the greatest antioxidant effect. Among amino-acids the best results are shown by methionine, leucine, isoleucine, and valine. Products obtained from certain amino-acids and dihydroxyacetone are far more effective than butoxyanisole. These results enabled compositions prepared from dihydroxyacetone and amino-acids such as alanine, leucine, histidine, methionine, phenylalanine, threonine, and tryptophan to be recommended as food antioxidants for oils and fats[88].

Glycine, alanine, lysine, ornithine, arginine, and glutamic and aspartic acids react with sugars (glucose, fructose, etc.) under certain conditions (pH 11−13 at 100−120°C) to give food colorants having an antioxidant effect, adsorbing oxygen, and inhibiting lipoxidase[89].

Cysteine is able to occupy a special position in the food industry because of its mercapto-group and hence specific physicochemical properties. Laboratory and industrial research on *L*-cysteine and *L*-cystine has shown that their introduction into many foodstuffs (meat and meat products, milk products, bread, farinaceous confectionery, etc.) has a considerable favourable effect. These amino-acids show great promise for stabilising the quality of foodstuffs—for slowing down enzymic browning reactions, stabilising ascorbic acid, retarding the autoxidation of fats, strengthening the effect of food preservatives, and also aromatising foodstuffs[90-97]. In Japan it is permissible to add cysteine as antioxidant to natural fruit juices. Cysteine is effective against the browning of foodstuffs, since it suppresses the formation of coloured compounds (melanoidins) by reducing intermediate products; or else free radicals formed from cysteine inactivate the intermediates. Since free cysteine is readily oxidised, it is normally used in the form of the relatively stable hydrochloride. During storage of a natural fruit juice ascorbic acid, being a reductant and hence opposing browning reactions, is gradually oxidised, with browning and decrease in the nutritional value of the product. This can be prevented by adding cysteine hydrochloride. A stable food antioxidant containing equimolecular proportions of ascorbic acid and cysteine has been patented[93].

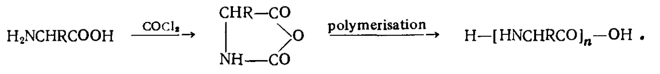
According to various authors cysteine as a reductant can also be used to improve the baking process (improve the rheological properties of the dough) and the quality of the bread[90,94–97]. Use together with ascorbic acid alone or mixed with potassium bromate gives a bread of improved structure, flavour, and aroma in a shorter time (this has already been introduced into practice in the USA, England, and Japan). Cysteine is considered to make the dough softer, by rapid reaction with gluten accompanied by cleavage of S–S bonds, while the oxidant slowly restores the elasticity, forming new S–S cross-links. Sulphur-containing amino-acids—methionine, *L*-cysteine, *L*-cysteinyl-*L*-cysteine—have been recommended for enriching phosphorylated starch, which serves as a gelling agent in foodstuffs and drinks[98].

The storage of perishable foodstuffs is one of the most important problems facing the food and canning industry. Glycine can be used to lengthen the storage life to fish products: addition of 1–2% (to improve taste and aroma) revealed that the growth of slime-forming bacteria was suppressed for some time. It is assumed that glycine inhibits biosynthesis of the cell walls of such bacteria, e.g. *Bacillus subtilis*[99]. A proposed deodorant for the oral cavity contains a reaction product of copper gluconate and glycine[100]. Derivatives obtained by the reaction of *L*-, *DL*- and *D*-glutamic acid with alkylamines and alcohols have been patented[101] for the protection of products from damage by micro-organisms. Increased storage life in the preservation of various foodstuffs—meat, fish, etc.—has been claimed[102] for the addition of a lauroyl-amino-acid (-leucine, -glycine). A method has been developed[103] for preserving foodstuffs by forming a coating from a prolamine and an amino-acid (alanine).

The list of amino-acids permitted as food additives in Japan comprises[104] *DL*-alanine, *L*-arginine-*L*-glutamate, sodium *L*-aspartate monohydrate, *L*-glutamic acid, sodium *L*-glutamate monohydrate, glycine, *L*-histidine hydrochloride monohydrate, *L*-isoleucine, *L*-lysine hydrochloride, *L*-lysine *L*-aspartate, *L*-lysine *L*-glutamate dihydrate, *DL*- and *L*-methionine, *L*-phenylalanine, *DL*- and *L*-threonine, *DL*- and *L*-tryptophan, and *L*-valine. Those permitted in the USA are[105] *DL*- and *L*-alanine, *L*-arginine, *L*-arginine hydrochloride, *DL*-aspartic acid, *L*-cystine, *L*-glutamic acid, ammonium *L*-glutamate, sodium *L*-glutamate monohydrate, potassium *L*-glutamate, *L*-glutamic acid hydrochloride, glycine, *DL*- and *L*-isoleucine, and *DL*- and *L*-leucine, *L*-lysine hydrochloride, *DL*- and *L*-methionine, *DL*- and *L*-phenylalanine, *L*-proline, *DL*- and *L*-serine, *L*-threonine, *DL*- and *L*-tryptophan, *L*-tyrosine, and *L*-valine.

III. USE OF AMINO-ACIDS IN THE SYNTHESIS OF POLYMERS

Polyamino-acids are usually obtained by the polymerisation of *N*-carboxyanhydrides prepared by the action of carbonyl chloride on the amino-acids:



Their skeletal structure resembles that of proteins, but their properties differ greatly from those of natural proteins, since they contain only one kind of amino-acid. Although various copolymers have already been synthesised, as yet they are of no practical value. Nevertheless, the structures of polyamino-acids are similar to those of such natural proteins as silk and leather, and therefore are regarded as suitable materials for the production of synthetic fibres and leather. Their use as raw material for synthetic fibres, films, and coatings of vinyl leathers was suggested by Woodward 20 years ago[7]; but these materials were then uneconomic as silk substitutes. Later glutamic acid became widely used in the Japanese food industry, and the development of methods for producing it more cheaply led to the use of polyglutamates as coatings for artificial leathers.

Poly(methyl *L*- and *D*-glutamate) are obtained by polymerisation of the *N*-carboxyanhydrides of γ-methyl *L*- and *D*-glutamates, prepared by treating the glutamates with carbonyl chloride in the presence of an appropriate polymerisation initiator in a suitable solvent[106–109]. The resulting polymer is soluble in halogenated hydrocarbons and has a highly regular linear structure, forming right-handed and left-handed α-helices from the initial *L*- and *D*-anhydrides respectively.

Two types of polymers based on γ-methyl glutamate (PGS—in the form of a solution in both cases, since PGS becomes insoluble after removal of the solvent, and moulding requires the direct use of a solution of the polymer)—unmodified PGS (commercial designation PLG) and modified PGS (PLG-N)[106–109]—which can be used e.g. for manufacture of artificial leather, synthetic fibres, and films for edible packings, are manufactured in Japan. Wet spinning gives a fibre closer than other synthetic fibres to natural silk in appearance and "feel", similar in strength and elongation, and surpassing it in resistance to weathering[107,110]. The practical value of PGS is evident in the usual application of an approximately 10% solution to coat the surface of vinyl leathers, which then become very closely similar to natural leather, highly resistant to heat, water, chemicals, and dirt, with good dyeability and several other valuable properties[109,111]. All this has resulted in the widespread use of such leathers in the manufacture of handbags, suitcases, furniture, clothing, and footwear.

Research on the preparation and properties of polyamino-acids is being vigorously pursued: polymerisation conditions[108,112,113] and effective moulding methods[110,114] are being worked out, and polymers based on other amino-acids—e.g. aspartic acid[111,115–117], glycine[115], alanine[118,119], and lysine[115,119,120]—have been synthesised. Many papers have appeared on the preparation of copolymers of amino-acids, which opens up great opportunities for modifying the properties of the resulting materials. The copolymer of γ-methyl *L*-glutamate with 1% of *L*-methionine, obtained from the corresponding *N*-carboxyanhydrides, will give a fibre of enhanced strength in comparison with the fibre without added methionine[121]. Several copolymers of *L*-leucine with *L*-cystine varying in composition and molecular weight have been synthesised[122], from which fibres have been obtained by wet spinning. X-Ray diffraction and infrared spectroscopy indicate that the fibres comprise α-helices with cystine bridges. The mechanical properties show strength and elasticity not inferior to those of wool. In contrast to wool fibres, however, whose modulus of elasticity increases appreciably at deformations > 20%, these synthetic fibres develop plasticity in this range of deformations.

Modification of poly-*D*-glutamic acid and poly-*L*-aspartic acid with styrene gives resins suitable for the production of a silklike fibre with enhanced alkali resistance[123]. Copolymers of *DL*-methionine and *L*-leucine form flexible films able to transmit water vapour slowly. Oxidation of the methylthioethyl groups by hydrogen peroxide to methylsulphonium groups strengthens the hydrophilic properties of these films, the rate of passage of vapour through a film increasing rapidly with the number of groups oxidised. The permeability of such films to carbon dioxide and oxygen is strongly dependent on the ratio of methionine to leucine. The above properties are of interest in connection with possible use of the films in various prostheses, in particular in artificial kidneys[124].

The main trend in improving the quality of synthetic polymeric materials is chemical modification of their structure. A great variety of materials having special properties, not present in the usual natural and synthetic fibres, can be obtained in virtue of the physical and chemical structural peculiarities of various modifications of polyamino-acids. Such properties include enhanced stability to chemical reagents and various physical factors, the ability to be resorbed in functioning tissues of the organism, etc. The modified polymers may find application in many branches of science and technology, such as medicine, foodstuffs, the pharmaceutical industry, etc. Films or fibres from polymers containing acid groups (poly-*L*-glutamic acid) modified with di-isocyanates become semipermeable and water-resistant, which is very important for their use in dialysis or surfery[125]. Threads for surgical sutures are obtained from readily hydrolysable fibre- and film-forming polymers based on amino-acids and hydroxy-acids[126] $[NH.CH(CH_3).COO.C(CH_3)_2.CO]_n$, $[NH.CH(CH_2C_6H_5).COO.[CH_2]_2.CO]_m$, etc.

A very important property of polyamino-acids is their non-toxicity and inertness towards the tissues of the macro-organism. On the other hand, the production of polymers possessing biological activity—antimicrobial, anti-inflammatory, anaesthetic—is of great interest. Polyamino-acids impregnated with bactericides, antiseptics, and antibiotics in various dressings and emergency remedies are very convenient for the prophylaxis and treatment of open wounds and skin diseases[127,128].

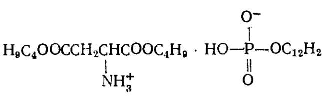
Medicinal preparations have recently become widely used in which coatings protect the contents of a tablet from the environment (moisture, air, light), prevent irritation of the stomach by mucosa by the medicinals, localise the action of the latter, etc. A protective coating for medicinal preparations has been developed from a copolymer of glutamic acid and an alkyl glutamate: it is odourless, sufficiently stable to the action of the gastric juices, and readily soluble in weakly acidic or neutral media[129].

Amino-acids and their derivatives can also fulfil various functions as additives to synthetic polymers and resins: they act as stabilisers, plasticisers, hardening accelerators, etc.[130-142] The copolymerisation of acrylonitrile (or methacrylonitrile) with $\alpha\beta$-unsaturated acids (e.g. itaconic) in the presence of glutamic acid and asparagine yields a water-soluble resin suitable as a binder or a modifier for paints and adhesives[130]. Because of their amphoteric character, amino-acids (glycine, lysine, aspartic acid) can be used to accelerate the hardening of phenol–formaldehyde resins[131]. To improve the resistance to sticking of goods from optically active γ-esters of glutamic acid, its *N*-substituted ethers may be added as plasticisers, possessing good compatibility with the base[132].

Glycine is used to increase the adhesion of silicone rubber to metal surfaces[136]. A γ-ethyl *L*-glutamate–*DL*-alanine copolymer coating has been proposed to eliminate tackiness, due to migration of the plasticiser, in moulded goods made of plasticised poly(vinyl chloride)[137]

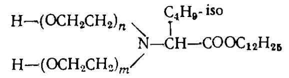
During recent years considerable attention has been paid in synthetic-fibre plants not only to the usual finishing methods (washing, removal of impurities, drying) but also to treatment of the fibres with surface-active agents, which confers optimum frictional properties. Amino-acid derivatives can be used for this purpose[138].

One of the most serious defects of synthetic and acetate fibres is their great tendency to become electrified, which increases the adsorption of dust and creates difficulties in use. Surface-active salts of diesters (e.g. butyl) of aspartic and glutamic acids with monophosphates containing a single higher alkyl group



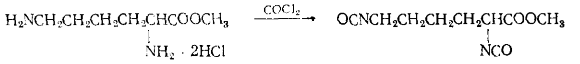
$$H_9C_4OOCCH_2\underset{\displaystyle NH_3^+}{\underset{|}{C}}HCOOC_4H_9 \cdot HO{-}\overset{\displaystyle O^-}{\overset{|}{\underset{\displaystyle O}{\underset{\|}{P}}}}{-}OC_{12}H_{25}$$

have been investigated for the purpose of lowering and removing the static charge on synthetic fibres. The electrifiability of nylon and polyester fibre was considerably diminished after treatment with a 0.4% methanolic solution of the quaternary ammonium salt formed by dibutyl aspartate with dodecyl hydrogen phosphate[139]. Amino-acid derivatives that dissolve readily in polyalkenes were prepared and studied with the aim of improving the antistatic properties of the latter. Thus the product of the condensation of dodecyl-leucine with oxiran



proved an excellent antistatic agent for polyethylene[140]. Derivatives of amino-acids may serve as antistatic agents for the most diverse synthetic polymers—polyamide, polyester, polyacrylonitrile, poly(vinyl chloride), polyalkene, etc.[141,142]

Finally, a very important possibility is the use of diamino-acids such as lysine and ornithine as raw material for polyamides or for the di-isocyanates employed in the manufacture of polyurethanes. The latter are obtained on the large scale by polymerising polyisocyanates (di- or poly-functional) and polyols containing at least two hydroxy-groups (e.g. glycols, polyethers, polyesters, etc.). They are widely used for the production of adhesives, foam plastics, protective coatings, and artificial leather. The action of carbonyl chloride on the dihydrochloride of the methyl ester of *L*-lysine in *o*-dichlorobenzene at 150°C followed by distillation yields methyl 2,6-di-isocyanatohexanoate, a liquid having a high boiling point[143]:



$$H_2NCH_2CH_2CH_2CH_2\underset{\displaystyle NH_2\cdot 2HCl}{\underset{|}{C}}HCOOCH_3 \xrightarrow{COCl_2} OCNCH_2CH_2CH_2CH_2\underset{\displaystyle NCO}{\underset{|}{C}}HCOOCH_3$$

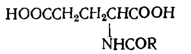
The decisive factor in assessing the toxicity of different di-isocyanates is their volatility. Being less volatile, the above di-isocyanate is less toxic than tolylene di-isocyanate, a fact of importance for the manufacture of polyurethanes.

IV. SURFACE-ACTIVE DERIVATIVES OF AMINO-ACIDS

Introduction of a hydrophobic moiety into one or other of the two hydrophilic functional groups in an amino-acid—amino and carboxy—will yield two types of surface-active compounds—anion-active and cation-active.

N-Acylamino-acids obtained by the action of chlorides of higher aliphatic acids belong to the first class. The initial amino-acids are most often aspartic (*N*-alkylaspartic) and especially glutamic (*N*-alkylglutamic)[144-147].

The surface tension, the film-forming and emulsifying power, and the pH of such surface-active compounds can be modified by varying the length of the carbon chain of the acyl group (usually C_{8-22}) and the number of alkaline components used to neutralise the carboxyls. The aliphatic acids most frequently employed are lauric, stearic, oleic, and palmitic. The best surface-active properties are possessed by *N*-acylglutamates[147,148]

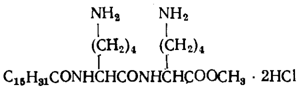


$$\mathrm{HOOCCH_2CH_2}\underset{\substack{|\\ \mathrm{NHCOR}}}{\mathrm{CH}}\mathrm{COOH}$$

aui acyl residue (C_8—C_{22}).

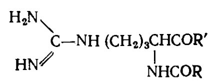
N-Lauroyl-*L*-glutamate salts exhibit better wetting, emulsifying, and dispersing properties than does the widely used sodium dodecanesulphonate[147]. The monosodium salt gives better results than does the disodium salt of the *N*-acylglutamate in model experiments with carbon blacks and powdered iron(III) and titanium(IV) oxides.

Esters of amino-acids obtained by the action of higher alcohols are cation-active surfactants, examples being the tetradecyl esters of glycine, serine, and aspartic acid, as well as dioctyl and dioctadecyl aspartates[149,150]. Cationic detergents, predominantly amines and quaternary ammonium salts, disturb membrane permeability and are highly active towards both Gram-positive and Gram-negative bacteria, which makes them useful in certain special applications, as disinfectants and antiseptics[151]. Several cationic surface-active derivatives of basic amino-acids, e.g. the hydrochloride of the methyl ester of palmitoyl-*L*-lysyl-*L*-lysine



$$\mathrm{C_{15}H_{31}CON H}\underset{}{\overset{\substack{\mathrm{NH_2}\\ |\\ (\mathrm{CH_2})_4\\ |}}{\mathrm{CH}}}\mathrm{CONH}\overset{\substack{\mathrm{NH_2}\\ |\\ (\mathrm{CH_2})_4\\ |}}{\mathrm{CH}}\mathrm{COOCH_3}\cdot 2\mathrm{HCl}$$

are also strongly bactericidal[152]. Arginine derivatives (their salts and esters) having the formula



$$\begin{matrix}\mathrm{H_2N}\diagdown & & \\ & \mathrm{C{-}NH(CH_2)_3}\underset{\substack{|\\ \mathrm{NHCOR}}}{\mathrm{CH}}\mathrm{COR'} \\ \mathrm{HN}\diagup\!\!\!\diagup & & \end{matrix}$$

RCO— acyl residue (C_8—C_{18});
$R'=OCH_3$, OC_2H_5, NH_2,

exert an antimicrobial and antifungal action, and can be used as disinfectant and antiseptic agents in dental powders, toothpastes, toilet lotions, etc.[153,154] The sodium salt of lauroylsarcosine, possessing a strong bactericidal effect together with good foaming power, is widely used in Japan for such purposes[7].

Amphoteric surface-active compounds have been prepared from alanine and from aspartic and glutamic acids[155]. A considerable number of publications have appeared on the possible use of surface-active derivatives of amino-acids in various wetting agents, emulsifiers, dispersants, bactericides, etc.[156-163] These derivatives merit special attention in connection with the growing contamination of the environment by industrial and domestic refuse, since they are biologically "soft", readily decomposed by bacteria under natural conditions. Wetting agents based on amino-acid derivatives, while possessing essentially the same wetting power as soap, do not have the two main defects of the latter: they are not harmed by acids or by hard water. Examples of possible applications of surface-active derivatives of amino-acids are given below. Thus wetting compositions in solid form have been proposed, containing as active component a salt of an *N*-acylated amino-acid[157]. Sodium, potassium, and ammonium salts of water-soluble amines are used, or salts of basic amino-acids, e.g. lysine or ornithine. *N*-Acylaspartic and *N*-acylglutamic acids can be employed both in optically active and in racemic forms. Several papers have appeared on the application of *N*-acylglutamates[158,159] and derivatives of aspartic acid[160,161] in cosmet products. *N*-Acyl-*N*-alkyl-β-alanine salts $RCONR'CH_2CH_2COOX$ (in which RCO represents a C_{8-22} acyl residue, R′ a straight-chain or branched C_{1-8} (cyclo)alkyl, and X hydrogen, an alkali metal, ammonium, or an aminoethanol or a bis- or tris-hydroxyethylamine radical) are present in wetting agents[162] and liquid shampoos[163] possessing good surface-active properties and foam-forming and wetting power.

Reaction of an aliphatic glycerol monester with glutamic (better with *L*-glutamic) and pyroglutamic acids under reduced pressure at 200°C yields odourless and tasteless surface-active compounds[164].

N-2′-Hydroxyethylglycines $HOCH_2CH_2NRCH_2COOH$ (where $R = CH_2CH_2OH$, CH_3, C_4H_9) have been recommended[165] as a base for detergents. From glycine have been obtained[138] new *N*-carboxymethylamides of perfluorocyclohexanecarboxylic acid $C_nH_{2n+1}ACONHCH_2COOH$, where A represents the perfluorocyclohexane ring and $n = 0-4$, whose sodium, potassium, or ammonium salts are used as surface-active agents in the polymerisation of fluorinated alkenes and of acrylates. They are present to the extent of 0.001–0.002% in polishing mixtures. The potassium salt of *N*-ethyl-*N*-perfluoro-octanesulphonylglycine has been introduced as a levelling agent into a liquid composition for cleaning floors[166], to ensure the formation of a semilustrous, polished, and dust-resistant film on the surface.

Detergent compositions on derivatives of aspartic acid (e.g. the sodium salts of *NN*-biscarboxymethylaspartic acid) are claimed[167] to possess the same cleansing power as those containing sodium tripolyphosphate. A proposed method for obtaining *N*-decanoylamino-acids and peptides (employed as surface-active and bactericidal agents) involves esterification of decanoic acid with 3-hydroxypyridine or 8-hydroxyquinoline followed by treatment of the esters with aqueous solutions of sodium or potassium salts of amino-acids or peptides[168]. A mixture of salts of *N*-alkanoylamino-acids (e.g. an *N*-alkanoyl-*L*-valine salt), an *N*-hydroxyalkylamide, and a salt of phenol [sic: "carboxylic acid salt" in Ref. 169—Ed. of Translation] gives a detergent composition of low toxicity and better wetting power than standard compositions[169].

V. OTHER FIELDS OF APPLICATION

1. Electrochemistry

Amino-acids have not yet found practical application in electrochemistry, apparently because of their high cost, but quite a number of patents have been granted on their possible use. They serve as complexing agents, and also have a good buffering effect on the electrolyte, thereby ensuring its stability and the production of high-quality deposits. The patent literature suggests that the use of amino-acids for the electrochemical production of various coatings and alloys has many advantages. Special attention has been paid to glycine[170-191], which increases the rate of electrodeposition by factors of 5–6 when present in the electrolytes. In the formation of a chromium–cobalt alloy glycine keeps the pH within the range 0.5–1;[170] its use in solution for the application of lead selenide coatings to dielectric materials makes it possible to obtain uniform, firmly adherent layers without activation of the substrate[171].

Good-quality palladium–nickel alloy deposits can be obtained only over a narrow range of current densities from an electrolyte containing palladium and nickel chlorides together with ammonia. This disadvantage is removed by adding glycine to the electrolyte[173]. The composition of the alloy and the deposition conditions in the presence of this amino-acid have been studied in detail[174]. Palladium-plating electrolytes can be based[175] on glycine and ethylenediaminetetra-acetic and diethylenetriaminepenta-acetic acids, which form palladium complexes differing in stability. The electrolytes are non-toxic and stable, enabling high-grade metal deposits to be obtained. The throwing power of the electrolytes has been studied, the physicochemical characteristics of the deposits are presented, the rules for obtaining high-quality deposits are elucidated, and electrolytes are proposed for palladium-plating (glycine content 44 g $litre^{-1}$). Good palladium deposits are obtained at a certain pH.[175]

Glycine is used together with Trilon B as a complexing agent in the deposition of nickel–tin[176] and nickel–tin–molybdenum[177] alloys. It serves as complexing agent in chemical nickel plating[178,179]. In the application of cobalt[180] and ruthenium[181] its use tends to stabilise the solution and diminish the porosity of the coating. In combination with cadmium oxide and ammonium chloride glycine increases the stability and the throwing power of the electrolyte used to obtain finely crystalline cadmium–tin alloy deposits[184]. Bright, dense chromium–cobalt alloy deposits, adhering well to the substrate and possessing high abrasion and corrosion resistance, can be obtained[185] from an electrolyte containing glycine and sodium dodecyl sulphate (respectively 50–250 and 0.05 g $litre^{-1}$). The electrolyte is stable in operation, and its composition can be adjusted by adding a previously prepared complex of the chromium compound and the amino-acid.

In a process for obtaining an iron–nickel–chromium alloy similar in composition to the chromium–nickel stainless steel Kh18N9 glycine is introduced into an electrolyte containing potassium chrome alum together with nickel and iron sulphates, in order to increase the buffer capacity of the electrolyte, raise the pH of hydration of chromium, and increase the thickness of the coating[186].

Glutamic acid hydrochloride is recommended for use with ammonium chloride at elevated temperatures below the melting point for the cleaning of gold alloys containing small quantities of tin, indium, germanium, antimony, and silicon[192]. A patent has appeared on the application of glutamic acid as a hydrotropic agent for increasing the throwing power of the electrolyte in the electrodeposition of zinc and other metals[193].

A chromium–nickel alloy can be obtained from an electrolyte containing the sulphates together with an amino-acid, e.g. cysteine[194]. This has great disadvantages over other processes, since chromium contents of 10–90% can be obtained depending on the electrolyte concentration and the electrolysis schedule. Furthermore, the proposed electrolyte enables this alloy to be obtained at room temperature, which improves the working conditions considerably. During recent years research has been undertaken in the USSR on copper-plating electrolytes containing various complexing and surface-active additives, including amino-acids, with the aim of replacing the poisonous and unstable cyanide electrolytes[195].

2. Photography

Reports have appeared on the possibility of using amino-acids in photography; mainly cysteine and cystine are recommended. To accelerate the one-stage photoprocess the amino-acids are introduced (together with 5-mercapto-1-phenyltetrazole as antifogging agent and ascorbic acid as accelerator) into the processing formulation containing metol, quinol, and sodium sulphite, carboxymethylcellulose, thiosulphate, and hydroxide. In the presence of 5-mercapto-1-phenyltetrazole cystine or cysteine improves the quality of the positive image, by increasing the maximum density and ensuring neutrality of tone[196].

Cysteic acid or a derivative can be added also for stabilisation purposes and to eliminate bronzing in the receiving layer of the positive material for the one-stage photographic process, which includes a latex—a copolymer of butadiene and methyl methacrylate—silicic acid, and an activator[197].

The use of cysteine hydrochloride has been patented as an agent for controlling the colour of images in developers not containing metol, amidol, *N*-benzyl-*p*-aminophenol, or *p*-aminophenol. Good results are obtained by the use of developers containing *NN*-diethyl-*p*-phenylenediamine, kojic acid, and cysteine hydrochloride in certain proportions[198].

Double salts of compounds $HS[CH_2]_nCH(NHR)COR'$ (where $n = 1-4$; $R = H$, or a lower or substituted acyl; and $R' = OH$, a lower acyloxy-group or a substituted amino-group) have been proposed to improve development and sensitometric characteristics in diffusion developers for half-tone print negatives[199]. The introduction of cysteine, its hydrochloride, cysteinylglycine, or *N*-methylcysteine hydrochloride into a devloper containing quinol as main component enhances appreciably the maximum density while preserving the same minimum density (fog) on development under the usual conditions[199]. Cysteine can also serve as chemical sensitiser of the negative or positive emulsion layer in the planographic printing plates employed in lithography[200].

Arginine and its salts have been suggested for rapid development of the latent image in a silver-halide emulsion film containing at least one developer[201]. Several surface-active derivatives of aspartic acid have been prepared and studied[202,203]. A series of *N*-alkyl-*N*-sulphosuccinyl derivatives of aspartic acid, possessing a branched structure and containing several hydrophobic and hydrophilic groups, show high wetting and emulsifying power. Disodium diethyl *N*-decyloxypropyl-γ-sulphosuccinylaspartate meets most closely the requirement for the washing of photographic emulsions[203].

3. Pesticides

Losses in agriculture due to pests, weeds, and plant and animal diseases are extremely high, approximately one-third of all agricultural production. Chemical plant-protection agents are widely used to diminish them, and intensive research is being undertaken to find new preparations, whose application is not only an important condition for eliminating the huge losses but also one of the most economic ways of intensifying agriculture[204]. Derivatives of such an important class of biologically active natural compounds as amino-acids have been the subject of numerous investigations on these lines. The demands on pesticidal preparations have increased sharply during recent years: they should not leave harmful residues in the environment, and their toxicity towards warm-blooded animals and man should be low. Amino-acids are of definite interest in this connection, since they are readily biodegradable, and their decomposition products are non-toxic.

The most diverse derivatives of many amino-acids have been investigated as weed-killers. Among all the known physiologically active compounds aryloxyalkanoic acids are the most highly active towards plants. Individual members of this group have found wide practical application as agents in the struggle against weeds (in high concentrations) and as growth stimulants (in low concentrations). Many derivatives of amino-acids have been described, one of the commonest herbicides in this series being 2,4-dichlorophenoxyacetic acid (2,4-D). These derivatives were obtained by reaction between the acetyl chloride and the amino-acid in the presence of sodium hydroxide or pyridine. When the herbicidal effect was tested, 2,4-dichlorophenoxyacetyl-*D*-amino-acids were found to be almost inactive, although the corresponding *DL*- and *L*-derivatives approached 2,4-D in activity[205,206].

Glycine derivatives that are nitrogen analogues of aryloxyacetic acids—*N*-2,4- and *N*-2,5-dichlorophenylglycines, *N*-2,4-dinitrophenylglycine, *N*-*o*- and *N*-*p*-chlorophenylglycines and *N*-phenyl-, *N*-*p*-hydroxyphenyl-, *N*-*p*-carboxyphenyl-, and *N*-1′-naphthyl-glycines—exhibit herbicidal activity. However, replacing the ethereal oxygen in phenoxyacetic acid by an imino-group lowers the activity by factors of 3–5.[205] Glycine often serves as initial compound for the production of herbicides, e.g. aminophosphonate[207] or *N*-phosphonomethylglycines[208].

Derivatives of *N*-benzoylalanine may serve as selective herbicides[209,210]. Novel amino-acid derivatives—*NN*-disubstituted alanines $R_nC_6H_{5-n}N(R'Y(COR''$, where R = Hal, Alk, AlkO, $n = 0-5$, R′ = Alkylene, R″ = Alk, AlkO, Ar, ArOAlkylene, and Y = COOH, *N*-mono- or *NN*-disubstituted NH_2CO—can be used[211] in any way known for herbicides, as solutions, dusts, and wettable powders, alone or mixed with other active components, with or without the use of surface-active dispersants or emulsifiers. A formulation containing a synergistic mixture of the ethyl ester of *N*-benzoyl-*N*-3,4-dichlorophenylalanine and 2,4-dichlorophenyl *p*-nitrophenyl ether has been claimed[212].

Substances used to remove leaves from various cultivated plants—termed defoliants—are closely related to herbicides. Not only compounds involved in the biosynthesis of *L*-lysine—pyridine-2,4-, -2,5-, and -2,6-dicarboxylic acids—but also *L*-lysine itself can form the basis of products that accelerate the fall of leaves from trees[213].

The action of amino-acid derivatives on the germination and growth of a plant depends on whether the latter is di- or mono-cotyledonous[214]. Thus *N*-benzoyl-*L*-aspartic acid and *N*-benzoyl-*L*-valine inhibit the germination of rice, and *N*-α-phthaloylacetyl-*L*-methionine retards that of horseradish. Phenacetyl-α-leucine slows down the early stage in the germination of dicotyledons, but does not affect monocotyledons. The mechanism of such inhibition is regarded as consisting in suppression of the action of lipase: the energy necessary for germination ceases to be supplied from the fats[215].

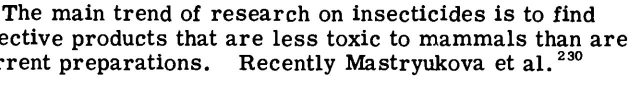
Several attempts have been made to use amino-acids as plant-growth regulators. Tryptophan, being a precursor of indolylacetic acid (a heteroauxin)—a true phytohormone—effectively accelerates the growth of plants[216]. *L*- and *DL*-Methionine, its metal (e.g. calcium and barium) salts, and its aliphatic (e.g. ethyl) esters have proved efficient growth stimulants for cucumbers, tomatoes, kidney beans, apple and orange trees, etc.[217] Watering cucumber seedlings with a solution containing proline together with uracil (each 1%) stimulates their growth and then increases the yield. A more concentrated solution of the same amino-acids (up to 30%) is a fertiliser for rice shoots[218].

Products containing *N*-purin-6′yl-*L*-phenylalanine, -cysteine, or -threonine as active component have been patented as new plant-growth regulators. Preparations based on these compounds prevent the decomposition of chlorophyll, increase leaf size, and accelerate plant growth[219]. Cysteine hydrochloride is a component of a preparation which stimulates the growth of maize, tomato seedlings, and fruit-tree saplings[220].

Many derivatives of amino-acids have been suggested as fungicides. Preparations based on glutamine derivatives $RNHCOCH_2CH_2CH(NHR)COOH$, where R = H or a lower alkyl, have been successfully used against diseases of citrus plants[221]. These products are non-toxic and are ineffective *in vitro*. Threonine and its *N*-formyl and *N*-benzoyl derivatives have the same effect[222]. The dodecyl ester of valine and other higher alkyl (tetradecyl, octadecyl, etc.) esters of various amino-acids have been patented as fungicides and bactericides for field-crop cultivation and horticulture[223,224].

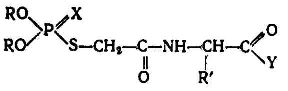
Investigation of the fungicidal action of higher aliphatic *N*-acyl derivatives of amino-acids (their sodium salts and methyl and ethyl esters) and of esters of amino-acids with higher alcohols has shown many of them to be effective *in vivo* against the most common disease of rice *Piricularia oryzae*, although they exhibit no activity *in vitro*; prophylactic use gives the greatest effect[224,225]. Since these amino-acid derivatives have low toxicity and are readily biodegradable, they fully deserve attention as agricultural chemicals that do not pollute the environment. It has been reported[226] that salts of alkylamines with such amino-acids as glycine, alanine, and pyroglutamic acid have proved effective against the diseases of rice. Several *N*-phenylacetyl- and *N*-naphth-1′-ylacetyl-amino-acids (derivatives of glycine, *L*-alanine, *L*-serine, *DL*-methionine, etc.) have been claimed[227] as bases for fungicidal preparations. Copper and nickel salts of amino-acids (valine, methionine, threonine, etc.) have been suggested[228] for use against diseases of citrus plants and rice. These salts are stable in water and have low toxicity towards warm-blooded animals; they are readily obtained by the action of copper sulphate and nickel dichloride respectively on the amino-acid in the presence of ammonia, an alkali-metal carbonate, or a strong base. In another patent[229] copper salts of *D*- and *L*-glutamic and *L*-aspartic acids or mixed copper salts of these acids and di- or tri-basic acids, such as phthalic or benzene-1,3,5-tricarboxylic acid, added to increase the stability of the preparations, are recommended for the struggle against duckweed and pathogenic fungi[229].

Glycine is used in the preparation of the thiadiazinethione fungicide tetrahydro-5′-methyl-2′-thionothiadiazin-3′-ylacetic acid, which satisfactorily suppresses nematodes, fungi, and weeds[204]:



The main trend of research on insecticides is to find effective products that are less toxic to mammals than are current preparations. Recently Mastryukova et al.[230]

have made detailed studies on a novel type of selective insecticides and acaricides comprising derivatives of phosphoro-thiolic and -thiolothionic acids containing residues of amino-acids, their esters, and their methylamides



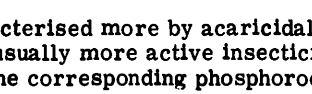
$X{=}O, S$; $Y{=}OH, OC_2H_5, NHCH_3$;

$R{=}CH_3, C_2H_5, NHCH_3$; $R'{=}H, CH_3$, iso-C_3H_7,

iso-C_4H_9, $CH_2C_6H_5$, n-C_3H_7, $CH_2C_6H_4OH$, $CH_2CH_2SCH_3$ etc.

The thio-organophosphorus compounds obtained, containing residues of acylated amino-acid derivatives, are either anticholinesterases (when $X = O$) or are converted into cholinesterase inhibitors by enzymic oxidation ($X = S$). The authors started from the view that the selectivity of such preparations may be based on differences in the sensitivity of arthropods and warm-blooded animals to the action of cholinesterase inhibitors and also on differences in the metabolic processes to which insecticides are subjected in the two types of organisms. In the first case it would probably be very significant whether or not the preparation is complementary to the active centre of the choline esterases or choline receptor. Examination of the physiological activity of these compounds showed that both their toxicity and their selectivity is strongly dependent on the nature of the amino-acids forming part of the molecule. Thus the β-alanine derivative ($R = C_2H_5$, $Y = S$) is a relatively strong insecticide comparable with Thiophos and a quite weak acaricide; the α-alanine derivative ($R = C_2H_5$, $R' = CH_3$, $Y = S$) is a strong acaricide (like Thiophos) and only a moderate insecticide. The corresponding valine derivative ($R = C_2H_5$, R' = iso-C_3H_7, $Y = S$) has still more marked acaricidal properties (twice as strong as Thiophos), but is almost devoid of insecticidal effect[230]. Derivatives of amino-acid methylamides ($Y = NHCH_3$) are more toxic to warm-blooded animals than are the corresponding esters. The selectivity of the action on arthropods is less marked in this series, although all the compounds are somewhat stronger acaricides. Great prospects are opened up for seeking selective preparations in this series[230].

Thio-organophosphorus compounds containing amino-acid fragments do not leave harmful residues in the environment, since the products of their decomposition and metabolism (acids of phosphorus, glycollic and thioglycollic acids, and biogenic amino-acids) are non-toxic. Methods have been developed for synthesising this series of compounds from salts of the corresponding thio-acids of phosphorus and chloroacylated derivatives of various amino-acids[231-233]. The same workers[234] investigated the analogous series of methylphosphonothiolothionates

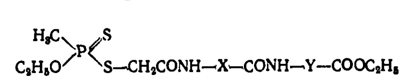


$R{=}H, CH_3$, iso-C_3H_7, iso-C_4H_9, $CH_2CH_2SCH_3$; $X{=}OH, OC_2H_5$

which are characterised more by acaricidal activity. However, they are usually more active insecticides and acaricides than are the corresponding phosphorodithioates and, of course, more toxic to warm-blooded animals. Thus changing from the dithiophosphate derivative of the ethyl ester of glycine to the corresponding dithiophosphonate involves increases in animal toxicity and in acaricidal and aphicidal effects by factors of 5.3, 40, and 30 respectively. The compounds obtained include active insecticides and acaricides having moderate toxicity towards animals[234].

Compounds obtained by adding dialkyl hydrogen thiophosphates to esters of *N*-acylated cysteine also possess insecticidal properties[235-237].

The next step on these lines was to study a series of derivatives of *O*-ethyl hydrogen methylphosphonodithioate containing in the detachable moiety of the insecticide a peptide fragment comprising residues of two amino-acids[238]



X and $Y{=}CH_2$, $CH_2{-}CH_2$, $CH(CH_3)$, $CH(C_3H_7$-iso$)$

on the assumption that formation of a dipeptide group in the side-chain may affect the specificity of sorption of these compounds by increasing the complementarity of the peptide fragment to the active centre of the enzyme[238]. Preparations of this series proved to be inferior to dithiophosphonates containing a single amino-acid residue, both in general insecticidal action and in selectivity, despite the slightly lower animal toxicity. It was concluded that further modification of the products with the accumulation of amino-acid residues was pointless[238].

In view of the rapidly increasing demands on pesticides, and also substantial difficulties involved in introducing them, the Reviewers feel that special interest attaches to the possible use of amino-acids as additives improving the properties of products already in use in agriculture. Thus it has been recommended to add aspartic acid and its salts to organophosphorus, organochlorine, and carbamate insecticides to stimulate the growth of the treated plants and remove the phytotoxic effect of the preparations[239]. Tryptophan stabilises the unstable cyclic *o*-hydroxybenzyl phosphate insecticides[240]. Arginine and its salts increase the solubility of the plant-growth stimulant gibberellin A_3 in aqueous solutions, which considerably expands the boundaries of its possible application[241]. Gibberellins may find practical application for the cultivation of ornamental plants and of grapes[204].

Derivatives of glutamic and aspartic acids may serve as stabilisers for dichlorovinyl dimethyl phosphate (DDVP, Dichlorophos), which during recent years has found widespread application in the fight against various harmful insects and mites in agriculture and public health[242]. Aspartic acid and methionine have been patented as stabilisers in fungicidal compositions[243].

The efficiency of insecticides is often enhanced by combination with attractants, which enable certain types of pests and the loci of infection to be detected in good time, so that measures can be taken to prevent their further dissemination. Use of such mixtures enables the resistance of insects to be overcome, eliminates the need to treat vast areas, diminishes the consumption of insecticides, and lowers the infectiousness of water, soil, and food products, while leaving certain useful species unaffected. The most common food baits are protein hydrolysates, whose mixtures with insecticides are employed against Eastern, Mediterranean, Natal, and Mexican fruit-flies, etc.[244] Addition of the protein hydrolysates increased the efficiency of the insecticides by factors of 3–12. The greatest effect was achieved by adding brewer's yeast or casein and yeast hydrolysates to the insecticides[244]. Many orders of insects, especially Diptera, respond to individual amino-acids, which apparently serve as nourishment. Glutamic acid is an effective attractant for the Mediterranean fruit-fly[244]. Lysine, while being an attractant for mosquitoes, attracts also Mexican, Eastern, Mediterranean, and melon flies. In the campaign against fruit-flies in the Hawaiian Islands it was observed that certain amino-acids are necessary for abundant egg-laying, which is promoted by acid and enzymic hydrolysates[244].

4. Motor-fuel Additives

To prevent the formation of deposits in the carburettors of interna-combustion engines it is proposed[245] to add to petrol 0.0005–0.1% of asparagine derivatives $R'NHCOCH_2.CH(NHR)COOH$, where R and R′ represent secondary and tertiary hydrocarbon radicals up to C_{22}. These compounds possess anticorrosive and dispersive properties, preventing carbonisation and icing[246–248]. Substituted amides of aspartic acid combined with succinates of diethylenetriamine, triethylenetetramine, and tetraethylenepentamine act as ashfree dispersing agents in the form of additives to hydraulic fluids[249].

5. Cosmetics

The buffering action of amino-acids, helping to maintain the normal functioning of the skin (by controlling the pH), the protective effect against bacteria, and the surface-active properties of amino-acid derivatives, as well as the favourable physiological action, have enabled amino-acids to be introduced into cosmetics.

In hair colorants it is recommended that ammonia could be replaced by arginine carbonate[250] or by glycine, *L*-alanine, or valine mixed with ammonium carbonate[251]. The use of 0.1–20% of arginine carbonate in hair-bleaching formulations diminishes the injury to the hairs while achieving the same bleaching effect as with formulations containing 9% of ammonium hydroxide[252].

Amino-acids are used in creams and hair conditioners as nutrients, improving the sheen and conferring softness. An especially favourable effect on hair is exerted by cysteine, on whose derivatives many papers have appeared in this connection. Like thioglycollic acid, cysteine and its derivatives can be used as reductants in cold[253,254] and permanent[255] waving. Derivatives or cysteine $RSCH_2CH.(NHR)COOH$ and methionine $RS[CH_2]_2CH(NHR)COOH$, where $R = HOCH_2CH_2$ or $NH_2CH_2CH_2$, have been proposed in various formulations ensuring a better, grease-free appearance of the hair[256]. Derivatives of cysteine and cysteamine may form the basis for shampoos against dandruff[257]. For the treatment of seborrhoea and other diseases characterised by enhanced secretion of sebum, formulations have been patented containing as active component the compound $RSCH_2CH(NH_2)COOH$ [where $R = (C_6H_5)_3C$, $(C_6H_5)_2CH$, $C_6H_5CH_2$, $HOOC[CH_2]_{2-4}$,[258] $HOOC[CH_2]_{1-2}$, and their salts with inorganic and organic acids)[259] or cystine derivatives[260]. Other patents have appeared on cysteine derivatives that can be used in cosmetics[261–263].

A proposed hair lacquer is based on salts (alkali-metal or amine) of poly-α-amino-acids (polyaspartic and polyglutamic)[122].

Great attention is paid in cosmetology to the so called natural moisturising factor (NMF).[7] It was shown not long ago that skin dryness is due not to loss of liquids from the horny layer, as had been thought previously, but to loss of NMF, which plays an important part in the retention of water. Since the main components of NMF are free glycine, threonine, alanine, aspartic and glutamic acids, serine, and pyrrolidonecarboxylic acid, the use in cosmetics of various amino-acids, their derivatives, and protein hydrolysates is based on control of the normal functioning of the skin. Patents have appeared on the application of enzymic hydrolysates of lactalbumin[264] and plankton[265], and on the use of condensates of amino-acids and sugars as nutrients and moisturising agents[266]. Amino-acids are present as moisturising and antiseptic agents in skin creams and toothpastes[153,154,267].

Aspartic acid and its derivatives have diverse applications in cosmetics[161,268–271]. Thus a salt of the acid can be used in photosensitive pigments for the treatment of keratodermatitis[269]. Addition to cosmetic preparations of aspartic acid or its derivatives together with vitamin B_6 is effective in preventing drying of the skin and for counteracting ageing[270].

A disadvantage of amino-acids with respect to their use in cosmetics is their hydrophilic character, which hinders their imbibition by skin. Their absorption can be improved by combining their use with alkaloids[272].

Surface-active derivatives of amino-acids can be applied fn the most diverse cosmetic products[149,150,154,158,163,268]. Derivatives of glutamic acid

$$M^+[OOCCH_2CH_2{-}CH(NHCOR)COO^-]H$$

where M = Na, Li, $(C_2H_5)_4N$ and RCO is a C_{12-18} aliphatic acyl, possess several cosmetically valuable properties[158]. Apart from the excellent wetting and foaming power, *N*-acylglutamates do not irritate the skin, since their pH of 5.5–6.5 is similar, whereas a solution of ordinary soap is slightly alkaline. They are more effective than the latter for hard water, have an antimicrobial effect, and readily undergo biological degradation without polluting the environment. Sodium acylglutamates are used as foundations or components in shampoos, detergents, etc. They can be usefully added to various domestic synthetic detergents obtained from petroleum or alcohols to mitigate their irritant action on the skin (e.g. in kitchen products). Detergent compositions containing salts of *N*-acylglutamic acids and betaines have a favourable action on skin and possess good cleansing power[159]. Butyl *N*-acylglutamates *L*-$RNHCH(COOC_4H_9)CH_2CH_2.COOC_4H_9$ (where R represents lauroyl, miristoyl, or stearoyl) are recommended for use in lip salve[273].

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The Formation of High-temperature Materials by Direct High-frequency Fusion in a Cold Container

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A new technology of the formation of high-temperature non-metallic crystals, glasses, and fused ceramic materials is described. It is based on the method of direct induction fusion in a cold container. An account is given of the physical foundations of the technology and the technological apparatus is described. The possibilities and advantages of the new technology in the synthesis of pure high-temperature compounds in melts, in the growing of single crystals of oxide compounds, and in the preparation of high-temperature glasses and polycrystalline fused ceramics are demonstrated. The properties of the new materials are described. The bibliography includes 83 references.

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I. INTRODUCTION

Single crystals, glasses, and fused ceramic materials based on non-metallic high-temperature compounds are widely used in modern engineering and industry. The components of optical apparatus, the working elements of lasers and masers, the refractory components of metallurgical apparatus and glass furnaces, the elements of electrothermal devices, electrodes, and insulating elements of magnetohydrodynamic current generators represent a by no means complete list of the applications of high-temperature non-metallic materials. In this review the term "high-temperature materials" is understood to include not only materials capable of operating at high temperatures (1500° C and above) but also materials obtained at a high temperature regardless of the temperature at which they are subsequently employed. Materials of this type include single crystals, glasses, and polycrystalline ceramics based on oxides, fluorides, nitrides, borides, and certain other compounds.

The technology of high-temperature materials is an independent branch of engineering with its own methods, apparatus, and unsolved problems. The latter include (1 the formation of new single crystals, glasses, and fused ceramics requiring for this purpose temperatures in excess of 2000° C, necessitating the development of fundamentally new technological processes; (2) the formation of single crystals with an ideally homogeneous crystal structure; this condition requires that the technological processes be performed with parameters effectively stabilised over a long period; (3) the formation of single crystals, glasses, and fused ceramics with high chemical purity; thus the majority of laser crystals and glasses must not contain admixtures of iron, copper, certain lanthanides, and certain other impurities in amounts exceeding $10^{-4}\%$, while glasses for optical fibre connectors must not contain certain optically active impurities in amounts greater than $10^{-6}\%$; this condition necessitates the development of special "pure" technological processes in which the initial specially pure reagents are not contaminated; (4) the formation of materials under specific oxidation-reduction condition; (5) the formation of such materials in large amounts with the minimum expenditure of natural resources—energy, water, etc., and also with the minimum amount of waste.

A particular difficulty faced by technologists does not arise from each of the individual problems described but from their combination. For example, a high temperature can be readily achieved in industrial arc fusion processes, but in this method of fusion it is difficult to maintain the chemical purity of the material, to establish the necessary oxidation-reduction conditions, and to ensure the stability of the crystallisation process. On the other hand, fusion with the aid of radiation beams fully ensures a high purity of the material and the required oxidation-reduction conditions, but it is impossible to obtain large amounts of the material. Other existing technological processes which serve as the basis of the synthesis of high-temperature materials can also be shown to have weak features. We shall examine, for example, the existing process for the growing of high-temperature single crystals. Single crystals are most frequently grown from the melt by the Czochralski method[1] involving drawing on a seed. An amount of the crystallisable substance is placed in a metallic crucible heated in a resistance furnace or by high-frequency currents. The crucible plays the role not only of the container but also of a heating body from which heat is transferred to the melt. This method yields many crystals used in modern engineering—the yttrium–aluminium garnet, ruby, leucosapphire, lithium niobate and tantalate, the gadolinium–gallium garnet, lanthanum fluoride, and many others. A weak feature of this technology is the crucible, the choice of materials for the manufacture of which is very limited. These are platinum-group metals: platinum (m.p.1769° C), iridium (m.p.2450° C), and platinum–rhodium alloys (m.p. 1769–1950° C). In a few instances it is possible to employ molybdenum (m.p.2700° C), tungsten (m.p.3400° C), or graphite. The material of the crucible must be more refractory than the material contained in it and it must not interact chemically with the melt and the atmosphere surrounding it. Unfortunately, none of the materials enumerated above possesses the entire set of the necessary properties and this creates serious obstacles to the development of the technology of high-temperature crystals. An analogous problem arises also in the technology of glasses and fused ceramic materials.

We believe that the technology discussed in this review may claim to provide a general solution to the problem of the formation of high-temperature materials from the melt. It is based on the method of direct high-frequency fusion in a cold container. The process includes three principal elements: (1) induction fusion of the substance by high-frequency currents; (2) the retention of the melt in a cold shell having the same composition as the melt; (3) initiation of the process by a special procedure—start fusion.

These elements have been proposed independently at different times by different investigators. Thus it was suggested in 1905 that metals be fused in a solid shell of the same metal[2]. The idea proved so fruitful that it initiated the wide-scale incorporation of garnissage fusion in pyrometallurgy. An electric arc, an electron beam, or a plasma flame were suggested as the energy sources for the fusion of the metal[3]. Induction fusion of the metal in a cold container was proposed later[4,5], but, for reasons which will be described below, this procedure was not introduced on a large scale. Attempts were also made to employ high-frequency fusion in a garnissage in order to obtain semiconductors[6,7]. The idea of employing induction heating in a shell of the solid phase also for high-temperature electrically non-conducting or weakly conducting (in the solid state) materials arose a comparatively long time ago. In 1961 Monforte[8] achieved the fusion of ferrites: Clark and Chapman[9] described the preparation of crystalline uranium dioxide blocks; the relevant patents have been published[10,11]. In the USSR an attempt of this kind was made[12] to obtain crystals of iron-containing garnets.

In the middle 1960's studies designed to create the technology of high-temperature materials based on direct high-frequency fusion, the development of the necessary apparatus, and the synthesis of individual materials were begun at the Lebedev Physical Institute of the USSR Academy of Sciences[13-15]. The first apparatus for the fusion of high-temperature non-conducting (in the solid state) substances become available at the Physical Institute at that time and the fundamental characteristics of the process were understood. At the same time the search was begun for conditions corresponding to the fusion and crystallisation of compounds of different classes fluorides, halides, oxides, and complex oxide compounds. The conditions for the preparation of single crystals, glasses, fused ceramic materials, including multiphase compositions, were investigated. Ruby and leucosapphire single crystals, grown by drawing on a seed became available; single crystals of stabilised cubic zirconium and hafnium dioxides (fianits) were obtained for the first time as well as small single crystals of scandium, yttrium, gadolinium, and erbium oxides. Many fused high-temperature compounds were obtained and their properties proved to be more effective than those of the analogous materials prepared previously by solid-phase synthesis. Among these mention must be made of compounds such as mullite, β-sodium-alumina, yttrium, lanthanum, and other lanthanide chromites, the titanates, zirconates, and hafnates of Group II and III elements, high-temperature glasses, and other materials. The first attempts already showed that the new technology has many advantages.

1. The process temperature has no apparent limitations and may reach 3000° C and above.

2. The absence of contact between the melt and chemically different substances guarantees a high "purity" of the process. The materials obtained have a chemical purity which is at least not inferior to that of the initial components. In many instances the purity actually proves to be higher, because volatile impurities such as the oxides of alkali metals, chlorides, nitrates, sulphates and certain others are burnt off at a high temperature.

3. The processes may be carried out in various gaseous atmospheres: in air, in oxygen, in hydrogen, in neutral gases, and also *in vacuo*, which makes it possible to establish various oxidation-reduction conditions and to carry out oxidative, reductive, or neutral fusion of the materials.

4. The process is very convenient for carrying out chemical reactions in the melt at high temperatures, for example, in the synthesis of complex oxide compounds. Virtually any type of chemical reactions with participation of a melt in both single-phase and heterophase systems can be achieved.

5. The fusion and crystallisation process can be carried out not only periodically but also continuously.

The sum of the above advantages shows that there are good reasons for devising a universal industrial process for the synthesis of high-temperature single crystals, glasses, and fused ceramic materials.

The reports published in recent years have shown that the new technique for the fusion of high-temperature materials is widely used both in the USSR[16] and abroad. For example, it appears that advances have been made in researches of this kind in the USA, where the fusion and crystallisation of zirconium dioxide[17] and certain other high-temperature materials have been achieved at the CERES Company under Wenckus' supervision and at the Bell Laboratories.

II. THE TECHNIQUE OF DIRECT HIGH-FREQUENCY FUSION IN A COLD CONTAINER. PHYSICAL PRINCIPLES, APPARATUS, AND ELEMENTS OF THE TECHNOLOGY

The theory of the heating of materials in an alternating electromagnetic field has been developed in detail[18-20]. Here we shall merely quote the conclusions of the theory, which will assist us in subsequent understanding of the characteristic features of the high-frequency heating of non-metallic high-temperature materials.

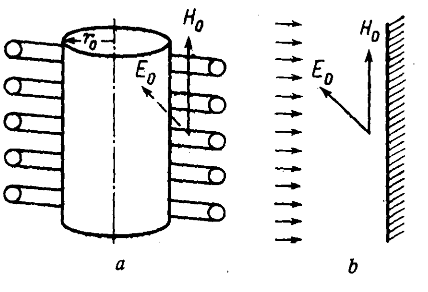

Figure 1. Schematic explanation of the heating of electrically conducting materials by high-frequency currents: *a*) semi-infinite cylinder in a cylindrical electromagnetic field; *b*) interaction of planar electromagnetic waves with a planar semi-infinite object.

Fig. 1 presents a typical scheme which explains the heating of electrically conducting bodies by a high-frequency current. A cylindrical body of the conducting material is in an alternating electromagnetic field with a cylindrical configuration established by a multiturn inductor. The efficiency of the heating of the cylinder depends on the nature of the energy of the high-frequency field absorbed and is determined both by the electrical and magnetic properties of the material, on the one hand, and the frequency of the alternating electromagnetic field, on the other.

In order to derive formulae relating the electric and magnetic field strengths in the material and the energy flux, on the one hand, to the electrical conductivity and the magnetic permeability of the substance, on the other, use is made of Maxwell's equations. The displacement current is neglected assuming that it is small compared with the conduction current. This approximation is undoubtedly valid for metals and is not unduly rough for the class of materials considered here. If the simpler case of the interaction of a planar electromagnetic wave with a planar half-bounded body (Fig. 1*b*) is considered, then, after transformation of Maxwell's equations and the conversion of the vector form into the coordinate form, it is possible to obtain the law governing the decrease of the amplitudes of the magnetic and electromagnetic field strengths:

$$H_{\mathrm{ampl}} = H_0 e^{-\frac{z}{\Delta}} \text{ and } E_{\mathrm{ampl}} = H_0 \frac{\sqrt{2}\, e^{-\frac{z}{\Delta}}}{\gamma\Delta},$$

where H_0 is the amplitude of the magnetic field strength on the surface of the body, z the distance from the surface (depth), γ the specific conductance of the body, and Δ a quantity characterising the attenuation of the amplitudes of E and H; the last quantity is equal to the thickness of the layer in which H_{ampl} and E_{ampl} diminish by the factor e and is called the depth of penetration. It has been shown that

$$\Delta = 5{,}03 \cdot 10^3 \sqrt{\frac{\rho}{\mu_r f}} \ (\mathrm{cm}), \qquad (1)$$

where ρ is the resistivity of the material, μ_r its magnetic permeability, and f the frequency of the electromagnetic field. The flux of the active energy in the body at a depth z also depends on Δ:

$$S_a = H_0^2 \frac{e^{-\frac{z}{\Delta}}}{2\gamma\Delta}. \qquad (2)$$

After substituting $z = 0$ and $z = \Delta$ in this formula, we find that the energy $S_{0a} - S_{\Delta a} = 0.864\, H_0^2/2\gamma\Delta = 0.864\, S_{0a}$ is evolved in a layer of material with a thickness Δ. This justifies the assumption in technical calculations that virtually the entire energy of the high-frequency field is absorbed in a surface layer with a thickness Δ.

We now return to the scheme in Fig. 1*a*. The law governing the attenuation of H, E, and S with increasing depth is derived in the same way as for the planar case (Fig. 1*b*) with the sole difference that the vector form of the equations is transformed into the coordinate form using a cylindrical coordinate system. In the "cylindrical" case the distribution of H, E, and S with respect to the radius of the cylinder at a specified field frequency f is no longer determined by the quantity Δ but by the ratio $r_0\sqrt{2}/\Delta$, where r_0 is the radius of the cylinder and Δ has the same significance as for the planar case. This makes it possible to tabulate data for the depth of penetration of fields into different materials. One should note that the depth of penetration of the electromagnetic wave into the cylinder is determined by the radius of the latter, apart from the properties of the material and the field frequency. One must therefore recall that Δ for a cylinder is not the true depth of penetration. It has been shown that, for $r_0\sqrt{2}/\Delta > 10$, the functions $H(r)$, $E(r)$, and $S(r)$ are of the same type as for the planar case. When $r_0\sqrt{2}/\Delta < 10$, special methods, which have been described in detail[18], must be used to derive the laws governing the distribution of H, E, and S in the cylinder. We shall not examine specific instances of the interaction of the high-frequency field with bodies having different configurations, since we should then inevitably enter the field of technical calculations, which is of only specialised interest (particularly since gross assumptions are made in these calculations, the main one being failure to take into account the finite length of the cylindrical body, i.e. failure to take into account end effects).

Table 1. Specific conductances of certain solid and fused non-metallic materials.

Compound	State	Temp., °C	Specific conductance, Ω cm	Ingot
LiF	melt	900	$1.2\cdot10^{-1}$	21
NaF	melt	1020	$1.9\cdot10^{-1}$	21
KF	melt	900	$2.6\cdot10^{-1}$	21
NaCl	melt	800	$3.3\cdot10^{-1}$	21
MgO	solid	2000	$5\cdot10^{2}$	22
SiO_2	solid	1700	$9\cdot10^{3}$	22
ZrO_2	solid	2000	1	22
Y_2O_3	melt	2430	$5\cdot10^{-2}$	23
Y_2O_3	solid	1500	$3\cdot10^{1}$	79
Al_2O_3	solid	1875	$2.2\cdot10^{4}$	22
Al_2O_3	melt	2200	$1\cdot10^{-1}$	24

In order to assess the possibility of the high-frequency fusion of non-metallic high-temperature materials (oxides, fluorides, halides, etc.), it is necessary to know the electrical properties of these materials in the solid state and in the melt. Since the vast majority of materials of this kind are non-magnetic, $\mu_r = 1$. Unfortunately the available literature data are extremely scanty. Table 1 presents the electrical conductivities of certain solids and fused non-metallic materials[21-24]. Evidently materials of the type in which we are interested have resistivities in the range 0.01–100 Ω cm at temperatures close to the melting point; on fusion, the conductivities of the materials increase, the increase being pronounced in many instances. It is also seen that at low temperatures their resistivities are 10^4–10^{14} Ω cm, i.e. they are effective dielectrics. Fig. 2a illustrates the temperature variation of the resistivity of alumina in the solid (corundum) and fused states, obtained in air[24]. Evidently the resistivity decreased on fusion by more than two orders of magnitude and amounted to 0.1 Ω cm in the melt. Fig. 3 presents a family of $\Delta = (\rho)$ curves for various electromagnetic field frequencies, calculated by Eqn. (1). Using Fig. 3, it is possible to determine the frequencies required to heat the chosen material. For example, a high-frequency generator with a frequency ranging from 500 kHz to 10 MHz should be used for an alumina melt; the depth of penetration then has reasonable values in the range 2.2–0.5 cm. Fig. 3 leads to the conclusion that the range of substances which can be fused by the induction method is restricted to those with resistivities in the melt of approximately 10 Ω cm. Otherwise the required frequencies are outside technically reasonable limits.

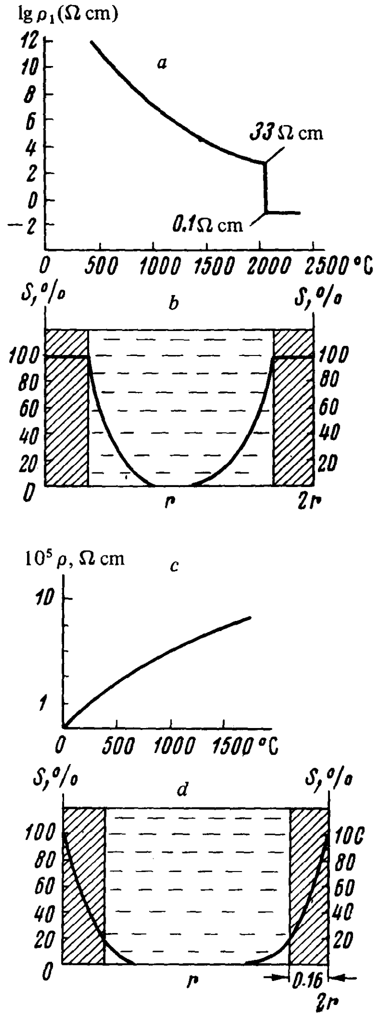

Figure 2. Temperature variation of the resistivity (ρ) and radial distribution of the energy of the high-frequency field (S) absorbed by a two-layer cylinder consisting of solid (outer shaded layer) and liquid (inner region) phases having identical chemical compositions: *a*) alumina; *b*) steel; *c*) Al_2O_3 cylinder, electromagnetic field frequency 5 MHz; *d*) steel cylinder, electromagnetic field frequency 2500 Hz.

The above discussion shows that (1) the melts of the majority of non-metallic high-temperature compounds can be effectively heated by high-frequency currents with the aid of accessible technical means; (2) the heating of these substances from room temperature to the melting point directly by the high-frequency field cannot be achieved.

We shall now consider certain characteristics of the direct high-frequency heating of non-metallic materials in a cold container which follow from the electrical properties of materials of this type. Fig. 2 compares typical temperature variations of the resistivities of a non-metallic material which is a dielectric in the solid state (Fig. 2*a*) and of a metal (Fig. 2*b*). The fundamental difference between these two types of materials is clear from the figures: in the first case the resistivity of the melt is lower by several orders of magnitude than that of the solid phase, while in the second case the resistivity of the melt is higher than that of the solid metal. Figs. 2*c* and 2*d* illustrate schematically for the two instances the nature of the absorption of the energy of the high-frequency field by a double-layer cylinder, the outer shell of which consists of the solid phase and the inner part is occupied by a melt having the same composition as the shell. This model reflects exactly the situation in which we are interested. Since the resistivity of the solid shell is lower than that of the melt in the case of the metal, it follows that, in conformity with Eqns. (1) and (2), it absorbs the major part of the energy of the high frequency field and shields the melt (Fig. 2*d*). The situation is different for a material with a "descending" temperature variation of the resistivity. Here the solid phase is in essence "transparent" to the electromagnetic field and does not prevent its penetration into the melt, while it is not itself heated by the field (Fig. 2*c*). Thus direct induction heating in a cold container is, as it were, specially designed for materials with a descending electrical resistivity–temperature curve and is relatively unsuitable for metals. In direct high-frequency fusion the metal melts in its entirety and a solid shell between the melt and the cold container does not remain, which naturally deprives this technique of its attractive feature—chemical purity; high-frequency fusion of non-metallic materials is free from this disadvantage. The "favourable" distribution of the power generated always leaves, between the melt heated to a high temperature and the cooled container, a layer of the solid phase unheated by the field where the entire temperature difference is "quenched". As will be shown below, this finding makes direct high-frequency fusion of non-metallic materials in a cold container energetically convenient.

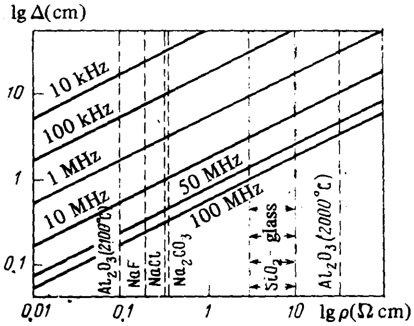

Figure 3. Family of $\Delta = \varphi(\rho)$ curves for various frequencies of the electromagnetic field.

Thus the high-frequency fusion of refractory dielectrics can be divided into two components: the heating of the material from room temperature to the melting point (which cannot be achieved directly by the induction method) and the maintenance of the substance in a fused state by supplying the energy of the high-frequency field. We shall examine the first component, the so called start fusion process (Fig. 4*a*). In the first place we shall determine the amount of the initial solid material which must be fused to enable the resulting melt to be heated by the field and grow in volume. A condition for its "viability" is the inequality

$$V \cdot P > K(T_m - T_0)\pi D^2, \tag{3}$$

where V is the volume of the starting melt, P the power absorbed by unit volume of the melt, K the coefficient of heat transfer from the melt to the heat exchanger (the cooling water), T_m the temperature of the melt, T_0 the temperature of the heat exchanger, and D the drop diameter. The heat of the phase transition is excluded from consideration, because the fusion process can be carried out in principle as slowly as desired. For a drop diameter D much smaller than the internal diameter of the container, the assumption that the specific absorbed power P remains constant is not unduly approximate. We obtain from formula (3) the expression

$$D > \frac{6K}{P}(T_m - T_0). \tag{4}$$

The above inequality shows that, for the specified electromagnetic field strength and electrical conductivity of the melt (they determine the value of P), the critical dimension of the drop of the melt depends mainly on the thermally insulating properties of the solid phase. Thus, having satisfied condition (4), we obtain a "viable" drop of the melt, which absorbs the energy of the high-frequency field and increases in size as a result of the fusion of the surrounding solid phase.

In order to answer the question whether the fusion process proceeds until the complete fusion of the entire solid phase or ceases at some stage, we shall examine the condition for phase equilibrium, i.e. for the spatial stability of the interface between the melt and the solid phase (Fig. 4*b*). Phase equilibrium implies that the temperature at any point on the interface is equal to the melting point (T_{fu}) and does not vary with time. The amount of heat given up by the melt to the solid wall (on the assumption of complete mixing of the melt) is $Q_1 = \alpha_1(T_m - T_b)F\tau$, where α_1 is the heat transfer coefficient, T_b the temperature at the boundary between the solid and liquid phases, F the heat transfer surface area, and τ the time. The amount of heat transferred through the layer of the solid phase with a thickness σ_s and a thermal conductivity λ to the heat exchanger is $Q_2 = (\lambda/\sigma_s)(T_b - T_0)F\tau$. In the steady state $T_b = T_m$ and $Q_1 = Q_2$. We then obtain $\alpha(T_m - T_{fu})(\lambda/\sigma)(T_m - T_0)$ or

$$\frac{\lambda}{\sigma_s \alpha} = \frac{T_m - T_{fu}}{T_{fu} - T_0}, \tag{5}$$

where $T_m - T_{fu} = \Delta T$—a quantity characterising the superheating of the melt. When $\Delta T \to 0$, we have $\sigma_s \to \infty$, which implies that the melt must be superheated in order to maintain the phase equilibrium. We shall assume that λ, α, and T_0 are independent of σ_s, whereupon

$$\sigma_s \Delta T = \text{const}. \tag{6}$$

It is seen from Eqns. (5) and (6) that the system responds by a decrease or increase of the thickness of the layer of solid phase to an increase or decrease of T_m. On the other hand, the complete fusion of the solid phase requires infinite superheating. Furthermore, any processes in the solid shell leading to a change in its thermal conductivity (for example sintering) disturb the phase equilibrium and require a change either in the temperature of the melt or in the thickness of the solid layer. The state of phase equilibrium is also influenced by the nature of the mixing of the melt, which determines the coefficient of heat transfer. The requirement for superheating, which determines the very existence of the melt in the scheme under consideration, constitutes a marked difference between the cold container and the heated crucibles usually employed: in the latter case the temperature of the melt may be made as close as desired to that of the melting point and in certain cases the melt is actually supercooled. The inevitable superheating of the melt in the cold container has certain important consequences in its crystallisation, particularly in the growing of single crystals (see below).

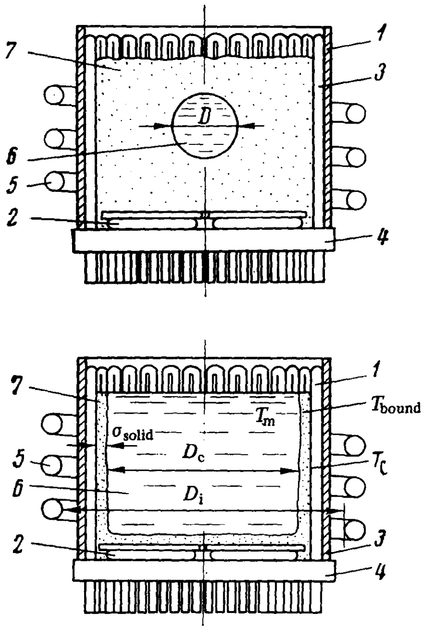

Figure 4. Schematic illustration of fusion (*a*) and of the state of equilibrium in the melt–solid system (*b*) in a cold container: 1) tubular water-cooled element; 2) water-cooled bottom; 3) insulating quartz cylinder; 4) retaining ring made of an insulating material; 5) inductor of the high-frequency generator; 6) melt; 7) charge.

We shall discuss further yet another important characteristic of the cold container–solid shell–melt system. We shall examine how the system responds to a decrease in the power ΔP absorbed by the melt (caused, for example, by the uncontrolled decrease of the power of the high-frequency generator). The decrease of the power immediately causes a decrease of T_m, which disturbs the phase equilibrium: the thickness of the solid shell begins to increase—the ratio of the diameter of the charge (D_c) to that of the inductor (D_i) diminishes. Under these conditions, either (1) a new state of equilibrium is established with a larger value of σ_S or (2) uncontrolled complete setting of the melt takes place. The point is that, with increase of σ_S, there is a simultaneous diminution of the diameter of the region of the melt which constitutes the charge in the inductor of the high-frequency generator; the coupling with the inductor diminishes at the same time. On the other hand, with increase of the thickness of the solid shell, the thermal insulation also increases and the heat flux from the melt in the cold container diminishes. The laws governing the decrease of the power absorbed by the melt and of the heat losses under these conditions are different. Figs. 5*a* and 5*b* represent schematically two possible versions of the response of the system to the decrease of the power of the generator. The result is to a large extent determined by the thermal conductivity of the solid phase: the higher the thermal conductivity the less stable the system. The occurrence of the spatial instability of the phase boundary during high frequency fusion of high-temperature non-metallic materials is a new factor which specialists working in the field of the high-frequency heating of metals did not encounter. This effect has a major influence on the apparatus and technological conditions in the fusion and crystallisation of specific high-temperature materials.

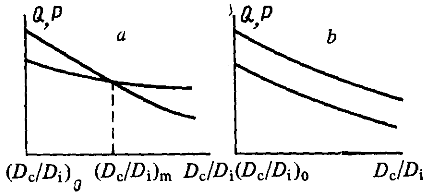

Figure 5. Response of the melt–solid phase system in a cold container to the decrease of the power of the generator: *a*) stable system; *b*) unstable system (D_m = melt diameter; D_i = inductor diameter).

Several types of apparatus have been developed at the Lebedev Physical Institute of the USSR Academy of Sciences for the direct high-frequency fusion and crystallisation of non-metallic high-temperature materials[13-15]. Each type of apparatus consists of a high-frequency generator with an oscillatory power ranging from 10 to 80 kW and a frequency from 1 to 13 MHz, a working chamber with water-cooled walls, a container, and a system for the stabilisation of the power of the generator and of the flow of cooling water. The high-frequency generator can be used in conjunction with both single-circuit and two-circuit schemes. Its characteristic feature is that it must be capable of stable operation at the maximum potential under the conditions of sharp changes in the charge: virtually in the range from its complete absence (at the start fusion stage) to the maximum charge. The working chamber serves to establish the required atmosphere (inert gas, reducing, or oxidising atmosphere). In order to maintain a constant average temperature of the melt and the phase equilibrium in the melt–solid shell system, devices stabilising the anodic potential (or the heater of the generator electronic valve) and the stream of cooling water are used.

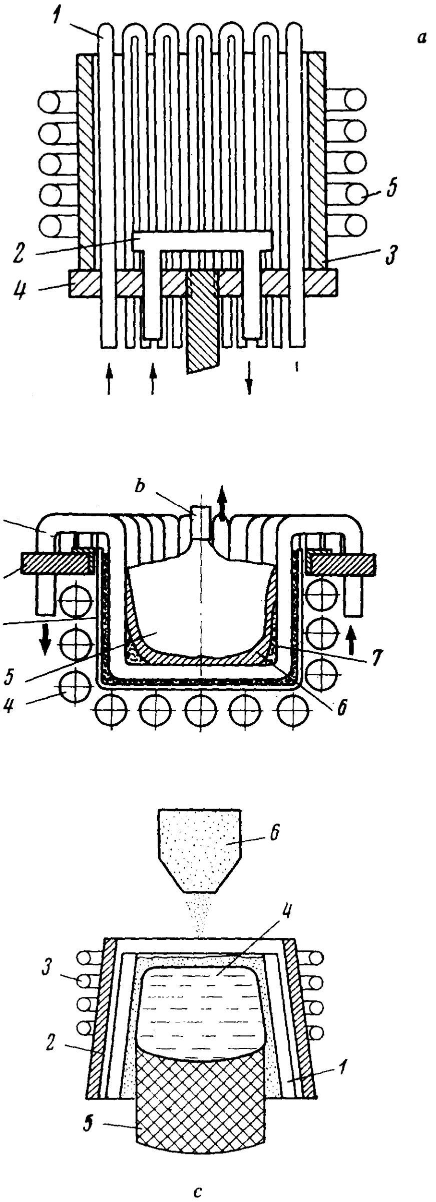

Figure 6. Design of cold containers: *a*) multielement cold container for the periodic fusion and crystallisation of refractory non-metallic materials [1) tubular water-cooled element; 2) water-cooled bottom; 3) insulating quartz cylinder; 4) insulating Micalex ring; 5) inductor of high-frequency generator]; *b*) multielement cold container for the periodic fusion and crystallisation of refractory non-metallic materials with a thermal conductivity in the solid state exceeding 6 W m^{-1} K^{-1} [1) tubular water-cooled element; 2) insulating Micalex insulating ring; 3) insulating quartz beaker; 4) inductor of high-frequency generator; 5) melt; 6) layer of crystallised melt; 7) charge; 8) growing crystal]; *c*) multielement cold container for the continuous fusion and crystallisation of refractory non-metallic materials [1) double-walled water-cooled conical container; 2) insulating quartz shield; 3) inductor of high-frequency generator; 4) melt; 5) block of crystallised material; 6) hopper with charge].

The design of the cooled container must meet a number of special requirements. In the first place, since the energy source is outside the container, the latter must be "transparent" to the energy. This means that it must be either made of a dielectric material or, when the container is made of a metal, must have slits which prevent the closure of circuits generating circular currents. Furthermore, the container must be made of a material with a high thermal conductivity and must be vigorously cooled with water (or another heat

Table 2. Compounds fused in a cold container.

Compound	M.p., °C	Compound	M.p., °C	Compound	M.p., °C
LiF	842	La_2O_3	2230	Lu_2O_3	2470
NaF	995	CeO_2	—	TiO_2	1855
CaF_2	1403	Pr_6O_{11}	2040	ZrO_2	2690
NaCl	800	Nd_2O_3	2315	HfO_2	2790
KCl	770	Sm_2O_3	2320	V_2O_5	670
MgO	2880	$Gd_2O_3^*$	2395	Nb_2O_5	1510
CaO	2585	Tb_4O_7	2330	Ta_2O_5	1877
SrO	2430	Dy_2O_3	2485	Bi_2O_3	817
BaO	1923	Ho_2O_3	2395	Cr_2O_3	2300
$Al_2O_3^*$	2046	$Er_2O_3^*$	2400	MnO_x	1700
$Sc_2O_3^*$	2405	Tm_2O_3	2390	Na_2CO_3	851
$Y_2O_3^*$	2410	Yb_2O_3	2420		

*Single crystals were obtained.

Table 3.

Compound	M.p., °C	Temp. of synthesis, °C
$Na_2O \cdot 11Al_2O_3$	1923	1970
$MgO + Al_2O_3 \rightarrow MgAl_2O_4$	2130	2300
$CaO + Al_2O_3 \rightarrow CaAl_2O_4$	1600	2300
$BaO + Al_2O_3 \rightarrow BaAl_2O_4$	2000	2300
$3Y_2O_3 + 5Al_2O_3 \rightarrow 2Y_3Al_5O_{12}^*$	1930	2100
$La_2O_3 + Al_2O_3 \rightarrow 2LaAlO_3$	2100	2300
$3Al_2O_3 + 2SiO_2 \rightarrow 3Al_2O_3 \cdot 2SiO_2$	1910	2100
$2Al_2O_3 + SiO_2 \rightarrow 2Al_2O_3 \cdot SiO_2$	1850	2100
$SrO + TiO_2 \rightarrow SrTiO_3$	2038	2200
$R_2O_3 + 2TiO_2 \rightarrow R_2Ti_2O_7^*$ (R = Sc, Y, La, Nd, Sm, Eu, Gd, Dy, Ho, Er, Tm, Yb)	—	2000—2300
$CaO + ZrO_2 \rightarrow CaZrO_3$	2345	2600
$Sc_2O_3 + 2ZrO_2 \rightarrow Sc_2Zr_2O_7^*$	2700	2900
$SrO + ZrO_2 \rightarrow SrZrO_3$	2470	2600
$La_2O_3 + 2ZrO_2 \rightarrow La_2Zr_2O_7$	—	2400
$SrO + HfO_2 \rightarrow SrHfO_3$	—	3000
$Y_2O_3 + Cr_2O_3 \rightarrow 2YCrO_3^{**}$	2290	2500
$MgO + Cr_2O_3 \rightarrow MgCr_2O_4$	2150	2300
$CaO + HfO_2 \rightarrow CaHfO_3$	2700	2900
$La_2O_3 + Cr_2O_3 \rightarrow 2LaCrO_3^{**}$	2430	2600
$CaO + MoO_3 \rightarrow CaMoO_4$	1449	1700
$SrO + MoO_3 \rightarrow SrMoO_4$	1468	1800
$CaO + WO_3 \rightarrow CaWO_4$	1580	1800
$SrO + WO_3 \rightarrow SrWO_4$	1566	1800
$ZrO_2 +$ (8-50 mole%) MgO, CaO, SrO, Sc_2O_3, Y_2O_3, La_2O_3, $TR_2O_3^*$	—	2700—2900
$HfO_2 +$ (8-50 mole%) MgO, CaO, SrO, Sc_2O_3, Y_2O_3, La_2O_3, TR_2O_3	—	2800—3000
$R_2O_3 - Al_2O_3 - SiO_2$ (R = Sc, Y, La, Nd, Sm, Eu, Gd, Tb, Er, Yb)***	—	1800—2400

*Single crystals were obtained.
**With an admixture of 5 wt.% $CaCr_2O_4$.
***Optically transparent glasses.

exchanger). Several types of containers made of dielectric materials (quartz glass) and various metals (copper, aluminium) were developed at the Physical Institute.

The containers illustrated in Fig. 6 proved to be the most suitable for the fusion and crystallisation of refractory non-metallic materials. One of them (Fig. 6*a*) makes it possible to fuse and crystallise a large number of different materials (Tables 2 and 3). In order to obtain crystals of materials whose thermal conductivity in the solid state is higher than 6 W m^{-1} K^{-1}, it is more useful to use a container of a different type (Fig. 6*b*), which makes it possible to supply energy not only from the lateral surface of the melt but also from below. The container illustrated in Fig. 6*c* is designed for the continuous fusion and crystallisation of materials.

Direct experimental determination of the efficiencies of the above types of apparatus showed that 50–60% of the electrical power supplied to the apparatus is evolved in the container with the melt.

The technological fusion process includes three stages. It begins with the formation of the "seed" melt, which, as stated above, can be achieved only by means of an additional source of heat. The following procedures have been used for this purpose: (1) fusion by supplying radiant energy; (2) fusion with the aid of flames; (3) heating and fusion by means of an electric arc; (4) fusion by introducing into the test substance an extraneous conducting material—the heating body. The most convenient method for the fusion of oxide and certain other types of materials is start fusion based on the use of small amounts (usually several grammes) of a metal whose atoms enter into the composition of the material to be fused: aluminium in the case of alumina, yttrium in the case of yttrium oxide, etc.[14] When the high frequency generator is switched on, the lumps of metal introduced into the charge are heated by the energy of the high frequency field and melt the surrounding charge. As fusion proceeds, the metal is oxidised by atmospheric oxygen and the resulting oxide mixes with the melt without contaminating it. After the critical volume of the starting melt has been exceeded under the influence of the high-frequency field, the entire charge gradually melts with the exception of the layer in contact with the cooled walls of the container. Fresh portions of the charge are added to the melt until the attainment of the required volume. This is the second, transitional stage of the process. As the charge melts, equilibrium is established, which may be maintained indefinitely. This is the third stage of the fusion process. When the high frequency generator is switched off, rapid mass crystallisation or vitrification of the melt takes place and polycrystalline ingots or glasses are obtained. On slow directed crystallisation of the melt by the gradual decrease of the power of the generator or slow lowering of the container with the melt relative to the inductor, it is possible to obtain large single-crystal blocks. Single crystals can also be obtained by drawing on seeds. The crystallisation and glass formation processes will be described in greater detail below in the sections devoted to specific materials.

III. THE COLD CONTAINER—AN EFFECTIVE CHEMICAL REACTOR

The most important element of the technology of high-temperature materials is the chemical synthesis of the compounds, since the majority of the materials are complex compounds: complex oxides, oxygen-containing salt-like substances, complex fluorides, and mixed or simple compounds into which admixtures have been introduced. In order to obtain single crystals, a glass, or a ceramic material, it is necessary to synthesise initially the required compounds from simple starting materials. As a rule, the synthesis is carried out by the method of solid-phase reactions. For this purpose, the starting materials in the form of finely dispersed powders are carefully mixed and then heated at a temperature below the melting point of the reaction product. The temperature is usually 0.5–0.7 of T_{fu}. The mechanism of chemical reactions in the solid phase is complicated[25]. However, regardless of the details, the diffusion of atoms of one of the components (or those of both components) through a layer of the solid reaction products is an inevitable stage. Diffusion coefficients in solids are usually small (10^{-6}–10^{-12} $cm^2 s^{-1}$), so that diffusion is a bottleneck in the solid-phase reaction, restricting its velocity.

Owing to the low rate of solid-phase reactions, the synthesis is long and it is difficult to bring the process to completion, so that the reaction product contains as a rule an admixture of the unreacted components, i.e. it is not homogeneous. In reactions in melts, diffusion is no longer a "bottleneck", because, firstly, its rate in liquids is much higher than in solids and, secondly, liquids can be vigorously stirred either forcibly or by convection, as a result of which the rate of reaction increases still further. Furthermore, liquid reaction products can be subsequently crystallised and their chemical purity and structural perfection can be thereby improved. Despite its obvious advantages, the synthesis of high-temperature compounds in the melt, particularly when compounds with $T_{\text{fu}} \approx$ 2000°C are concerned, is used to a very limited extent. One can mention only a few studies where synthesis in a melt was carried out using a solar furnace[26,27], a rotating plasma furnace[28], or arc furnaces[29].

As already pointed out in the introduction, a cold container in which the melt of the initial substances or reaction products is heated by high-frequency currents can serve as an extremely universal and at the same time "clean" high-temperature chemical reactor. Using this technique, we were able to synthesise many complex oxides. Together with the reaction equations, these compounds are listed in Table 3. Most of the reactions enumerated are coupling reactions and take place in a homogeneous system. However, some of these are of the combined type: together with the interaction of the liquid components, there is a heterogeneous reaction involving the components of the gaseous atmosphere. A relevant example is provided by the solid solution of zirconium and hafnium dioxides which were synthesised[15] and then stabilised by lanthanide or variable-valence transition metal oxides. The rate of the reaction and the form of its products vary as a function of the composition of the gaseous atmosphere. Another example of a combined reaction is the synthesis of solid solutions of yttrium, lanthanum, and other lanthanide chromites with an admixture of magnesium, calcium, strontium, and barium chromites. Depending on the atmosphere, the electrical conductivity of these substances varies sharply.

The study of the kinetics of coupling reactions in melts showed that the chemical interaction of the initial components proceeds at a rate equal to the rate of solution of the particles of the solid components (lumps) in the melt of the reaction products, i.e. actually at the rate of fusion. The rate of fusion in typical instances is 0.1–1.0 kg min^{-1}, depending on the superheating of the melt, its viscosity, and the heat of the phase transition on fusion of the components. Thus the homogeneous chemical equilibrium in the systems which we investigated is established over a period ranging from several seconds to several minutes. The study of the reaction products by X-ray diffraction, microscope, electron microscope, and spectroscopic methods has invariably shown that, for a strictly stoichiometric composition of the initial mixture of components, the content of the latter in the final product does not exceed 0.01–0.1 vol.%. The kinetic curve for the synthesis in the melt (curve *2*) is compared in Fig. 7 with the corresponding curve for the solid-phase synthesis (curve *1*); the comparison evidently favours the synthesis in the melt.

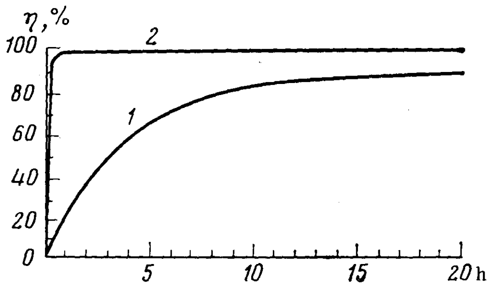

Figure 7. Kinetic curves (yield of reaction product η plotted against time): 1) for reactions in a mixture of three solid phases: $CaCO_3 + Fe_2O_3 \rightarrow CaFe_2O_4$; 2) for the reaction in the melt[25] $CaO + ZrO_2 \rightarrow CaZrO_3$ (the authors' data).

The situation is somewhat more complex in heterophase reactions, where the fused substance reacts with the gaseous atmosphere. Here it is necessary to examine two limiting cases.

(1) The active component of the gaseous atmosphere is insoluble in the melt. In this case the contact surface is restricted to the open surface of the melt. The rate of reaction is limited by the diffusion of gas molecules through the interface and the diffusion of reaction products in the bulk of the melt if the melt is not stirred or if the rate of stirring may be neglected. The viscosity of the melt therefore plays an important role here. The dependence of the rate of equilibration on the viscosity of the melt is clearly revealed when the rates of combustion of the starting metal and the reduction products in melts comprising lanthanum oxide, mullite ($3Al_2O_3.2SiO_2$), and the glass $La_2O_3.Al_2O_3.6SiO_2$ are compared. The viscosity of the melt increases sharply on passing from La_2O_3 to $3Al_2O_3.2SiO_2$ and particularly to a glass. In full conformity with this finding, the rates of combustion of metallic aluminium and the reduction products dispersed in the bulk of the melt are very different. Aluminium is combusted in 5–10 min in the La_2O_3 melt and in 15–20 min in the mullite melt; in a glass melt aluminium is not combusted after 10 h at 2000° C.

(2) The active component of the gaseous atmosphere is soluble in the melt; the rate of the heterophase reaction is then no longer limited by the rate of diffusion of the reaction products. An example of heterophase reactions with vigorous dissolution of the gaseous component is provided by the oxidation of the reduction products and metallic aluminium in Al_2O_3, $YAlO_3$, $Y_3Al_5O_{12}$, $MgAl_2O_4$, and certain other melts. It has been established experimentally that the melts of these substances dissolve large amounts of gaseous oxygen[30]. Thus a melt of alumina in contact with air dissolves more than 40 vol.% of oxygen. In this case the heterophase equilibrium is established after 5 min for a volume of the melt of 0.5 litre. When melts crystallise rapidly, the dissolved oxygen is evolved vigorously, the melt "boils", and the solidified block is threaded by a large number of large pores.

IV. THE FORMATION OF SINGLE CRYSTALS. THE GROWING OF LEUCOSAPPHIRE AND RUBY CRYSTALS

The growing of crystals from a melt in a cold container has many characteristic features compared with the usual method where they are grown in heated crucibles (the Czochralski, Stockbarger, Kiropoulos, or zone crystallisation methods). We shall consider these characteristics in connection with the method of crystallisation of the melt.

The Growing of Crystals by Drawing on a Seed

When crystals are grown by drawing on seeds (in the usual version this involves the Czochralski method) the following conditions must be observed: (1) a strictly defined distribution of temperature in the melt and in the crystallisation front must be established, namely the temperatures in the crystallisation front, i.e. in the middle part of the surface of the melt, must be lower than at any other point in the melt and (2) the temperature in the crystallisation front must be effectively stabilised. Convective streams in the melt play a major role in the distribution of temperature. Figs. 8*a* and 8*b* present photographs of the convection patterns on the surfaces of Al_2O_3 and $3Al_2O_3.2SiO_2$ melts in a cold container. The nature of the pattern depends on the generator frequency, the electrical conductivity of the material, the superheating and viscosity of the melt, and its diameter. The first pattern is typical of the majority of melts which we have investigated. The appearance of an irregular pattern, varying with time, is caused by the bulk-phase nature of the heating owing to the comparatively large depth of penetration by the high frequency field.

The required radial temperature gradient and stabilisation of the convection pattern were achieved by increasing the frequency and the diameter of the melt. Fig. 9 presents a plot of the distribution of temperature on the surface of an Al_2O_3 melt 80 mm in diameter at a field frequency of 5.28 MHz. Evidently in this case the radial temperature gradient satisfies the condition for the growing of crystals by drawing on a seed. However, here too the fluctuations in convective streams over a period of time remain significant. The majority of melts which we obtained had a low viscosity and only some of them, whose compositions incorporated glass-forming components such as SiO_2, were viscous. The absence of a convection pattern on the surface of the $3Al_2O_3.2SiO_2$ melt (Fig. 8*b*) is encountered rarely and is due to the high viscosity of the melt.

The possibility of growing crystals by drawing on a seed depends on the temperature of the melt and the thermal conductivity of the crystal. For normal crystal growth from the melt, it is necessary that the temperature of the latter at the crystallisation front, i.e. under the crystal, should be lower than at other points on the surface of the melt (Fig. 10). This requires that the heat loss from the surface of the melt under the crystal (Q_1) should exceed the heat loss from the open melt surface (Q_2). At high temperatures Q_2 is determined mainly by the radiation from the surface. Q_1 for "grey" bodies, such as the majority of refractory crystals at a temperature close to the melting point, is determined by the thermal conductivity of the crystal. Normal crystal growth is possible only for $Q_1 > Q_2$; otherwise uncontrolled crystal growth in the tengential direction begins. This effect is encountered in the growing of high-temperature crystals by the Czochralski method. In the case under consideration the situation is aggravated by the fact that, firstly, the melting points of the materials are in many cases 2000° C and above and, secondly, by the fact that, owing to the very essence of the method, superheating of the melt is needed. All these factors lead to considerable radiation losses from the surface of the melt, the attainment of the condition $Q_1 > Q_2$ is hindered, and uncontrolled tangential crystal growth results.

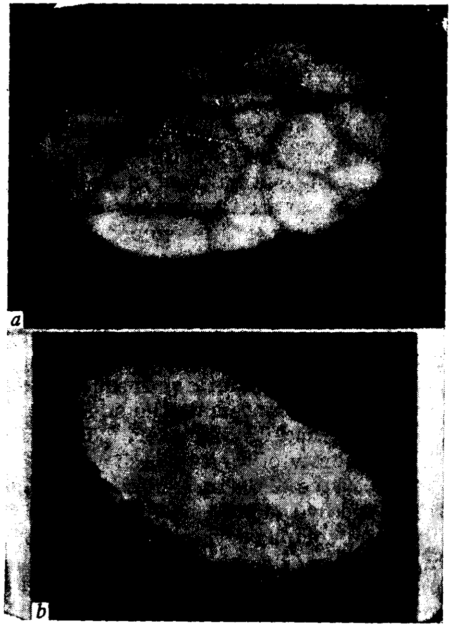

Figure 8. Convection patterns on the surface of the melt: *a*) Al_2O_3; *b*) $3Al_2O_3.2SiO_2$ (mullite).

The Growing of Crystals by Lowering the Crucible

In this case the growing of crystals in a cold container also differs significantly from that in the usual "hot" crucible by the Stockbarger–Bridgman method. The point is that, over the entire interface, the melt is in contact with a polycrystalline phase having the same composition. When the temperature of the melt is reduced, its crystallisation begins immediately at numerous nuclei already present. In this case it is almost impossible to grow a single crystal, since directed crystallisation of a large number of blocks takes place. However, as the growth of crystals proceeds in a large volume of the melt, the number of crystal blocks diminishes owing to selection by virtue of the different rates of growth and, after the complete crystallisation of the melt, the ingot is found to consist of a not unduly large number of single crystals. Thus it is possible to obtain small but quite perfect Sc_2O_3, Y_2O_3, Al_2O_3, and $Y_3Al_5O_{12}$ crystals as well as those of certain other compounds. Best results were achieved when single crystals of stabilised cubic zirconium and hafnium dioxides were grown by this procedure (see below).

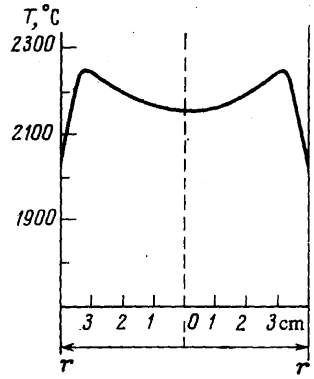

Figure 9. Radial temperature gradient on the surface of an alumina melt.

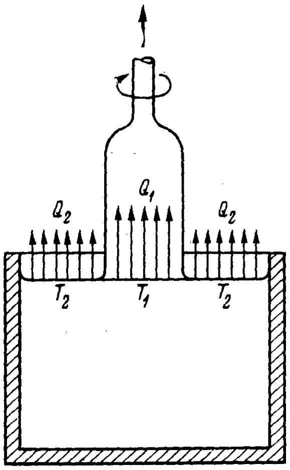

Figure 10. Schematic explanation of the nature of the thermal field in the zone of crystal growth by the Czochralski method.

Growth from Solution in the Melt

When crystals are grown from solutions in melts, the melt is highly superheated in the initial stage. This makes it impossible to employ the cold container technique in its pure form, since the solid shell fuses because of the identity of its composition with that of the melt. The difficulty may be overcome by employing the method used for the first time to grow semiconductor crystals[31], where the solid shell consists of a cylinder, pressed beforehand, of material having the same composition as the crystallising material (Fig. 11). In this case the saturated and superheated melt is in equilibrium with the solid shell. On the other hand, if the temperature at the solution–solid shell interface is non-uniform at different points, there is a possibility of the transfer of material from hotter to colder regions via the gradual dissolution of the shell and crystallisation of the dissolved material on the nuclei in the colder part of the volume (Fig. 11). Thus crystals may be grown from solutions in melts heated to temperatures much higher than are permitted by the platinum crucibles employed in processes of this kind (~ 1400–1500° C). The chemical corrosiveness of the melt does not play a role in this case. In a broader sense this technique can be used not only for crystallisation but also for the synthesis of substances in heated melts via coupling, substitution, exchange, etc. reactions.

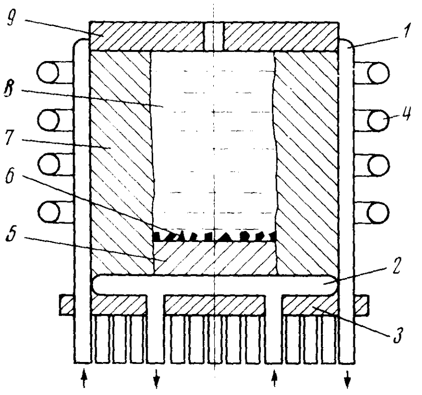

Figure 11. Schematic illustration of crystallisation from solution in a melt in a cold container: 1) tubular water-cooled element; 2) water-cooled bottom; 3) retaining ring of insulating material; 4) inductor of high-frequency generator; 5), 7), and 9) polycrystalline ceramic material having the same composition as the charge; 6) crystals; 8) melt.

The Growing of Sapphire and Ruby Crystals[32-35]

The growing of leucosapphire and ruby crystals in a cold container is to a large degree determined by the following factors: (1) the relatively low electrical conductivity of the Al_2O_3 melt; (2) its low viscosity; (3) the high solubility of gaseous oxygen in the melt; (4) the high thermal conductivity of solid corundum. The first two features lead to the formation of a fluctuating convection pattern generated by the variations in temperature at the crystallisation front. The third feature results in the evolution of oxygen at the boundary with the solid phase during the crystallisation of the oxygen-saturated melt. As a result, under the conditions of small temperature oscillations, small oxygen bubbles are incorporated in the growing crystal and give rise to light scattering regions.

On the one hand, the high thermal conductivity of corundum stabilises the crystal growth, ensuring a rapid removal of heat and preventing tangential growth, and, on the other hand, there is rapid removal of heat from the melts through the solid shell to the cold container, which leads (together with the low value of the specific power absorbed by the Al_2O_3 melt) to spatial instability of the interface between melt and the solid shell and to the necessity for high degrees of superheating of the melt. In order to attain prolonged stable growth of sapphire and ruby crystals, we therefore used the containers and inductors illustrated in Fig. 6*b*. This configuration of the container ensures uniform heating of the melts not only from the sides but also from below[14]. Fig. 12 presents a photograph of a growing sapphire crystal. The crystal diameter was regulated by altering the positions of the mobile shields located over the melt. The rate of drawing was 10–30 mm h^{-1} and the rate of rotation varied from 20 to 140 rev min^{-1}. In those cases where the convection pattern fluctuated markedly planetary rotation of the crystals was achieved by means of a special mechanism. During such rotation, the crystal intersects a large number of regions at different temperatures and the temperature of the front is averaged out; optical inhomogeneities associated with the entrainment of oxygen bubbles accordingly disappear. The crystallisation front in such crystals is virtually planar.

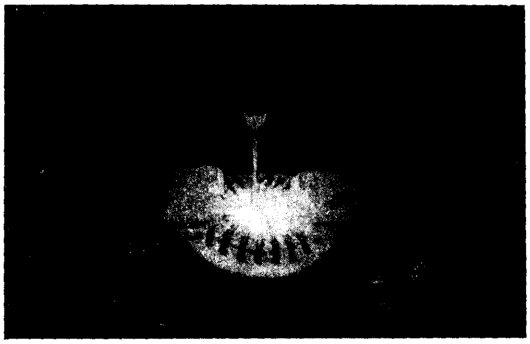

Figure 12. Photograph of a growing sapphire crystal.

Single crystals of sapphire and ruby with different orientations, up to 160 mm long and up to 35 mm in diameter, were obtained in this way. The crystals have characteristics which follow from the specific features of their preparation. The density of the dislocations in the basal plane was 10^2–10^3 cm^{-2}. A planar crystallisation front leads to a uniform radial distribution of chromium atoms in the ruby crystal. The distribution of chromium along the length of the ruby crystals was inhomogeneous: during the drawing process, the concentration of chromium fell, which is associated with the decomposition of chromium oxide in the melt during its superheating. In order to equalise the concentration of chromium over the length of the crystal, the melt was provided with a programmed "supplementary supply" of powdered chromium oxide from a special bunker was used.

V. THE PREPARATION AND PROPERTIES OF CRYSTALS OF STABILISED CUBIC ZIRCONIUM AND HAFNIUM DIOXIDES (FIANITS)

The monoclinic zirconium and hafnium dioxide crystals, obtained from solutions in the melt, have already been described[36]. The preparation of these crystals by the hydrothermal method is described in another communication[37]. In both cases small crystals several millimetres in size were obtained. The high melting points (Table 2), polymorphic transformations, and the high chemical corrosiveness of the melts precluded the growing of the crystals of these oxides from the melt. We developed a method for obtaining crystals of stabilised cubic zirconium and hafnium dioxides (fianits) from the melt[13,15,38]. The initial components (ZrO_2 and HfO_2) were of "specially pure" grade. The stabilising components were magnesium, calcium, strontium, barium, scandium, yttrium, lanthanum and other lanthanide oxides at concentrations up to 40 mole %.

The charge was placed in a water-cooled copper container (Fig. 6*a*), metallic zirconium, hafnium, or yttrium being used for the start fusion. The crystals were grown at 3000° C by the slow lowering of the container with the melt relative to the inductor. The growth time was 8 h. 1.5–6 kg of single-crystal blocks, up to 8 cm long and with a cross-sectional area up to 10 cm^2, was obtained simultaneously on our apparatus (Fig. 13). The crystals grown in this way were then annealed in vacuum or gas furnaces.

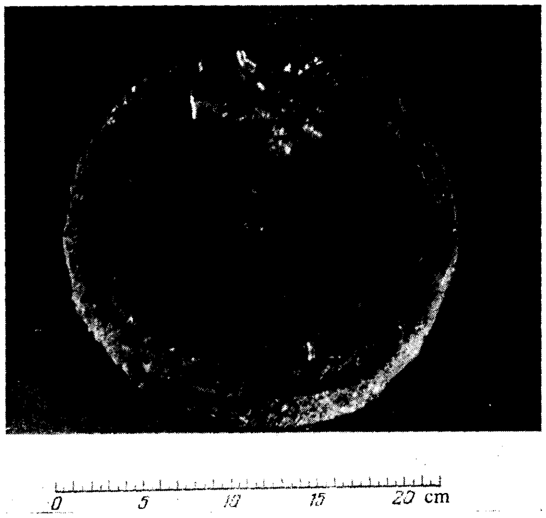

Figure 13. A block of zirconium dioxide crystal.

The Structure of the Crystals

The X-ray diffraction analysis[39] was performed on a DRON-0.5 apparatus using CuK_α radiation. The lattice constant of the crystals of stabilised zirconium dioxide was determined to within 0.001 Å from the (531) peak. The degree of order in the structure was characterised by the ratio of the intensities of the (600) and (200) lines and the normalised widths of the (531) peaks at the level of half their height. According to the results of the X-ray diffraction analysis, the crystals stabilised by X_2O_3 consisted in the main of the stabilised high-temperature crystal form with a cubic lattice of the fluorite structural type. The space group was $^5O_h - Fm3m$. Fig. 14 presents the experimental and calculated lattice constants and the number of vacancies in ZrO_2 as a function of the concentration of the stabilising oxide. The calculation was based on the hypothesis of close-packed spheres of different radii and the following formula was used:

$$d = 2.31\left(R_{Zr} + R_O + \frac{2m\Delta R}{100+m}\right), \qquad (7)$$

where d is the lattice constant, R_{Zr} and R_O are the radii of zirconium and oxygen ions (0.81 and 1.40 Å) respectively, m is the concentration of Y_2O_3 (mole %), and ΔR the difference between the radii of yttrium (0.90 Å) and zirconium ions. Eqn. (7) and the plots in Fig. 14 show that the concentration dependence of the lattice constant is not linear. The diffractometer traces for the specimens with 6 mole % Y_2O_3 contain split lines which, together with the deviation of the lattice constant towards higher values, shows that these specimens include both cubic and distorted tetragonal phases. Naturally, under these conditions the Y_2O_3 concentration must be referred solely to the cubic phase, which results in an increase of its lattice constant to 5.136 Å. The content of the tetragonal phase in the specimens can be estimated from these data: it amounts to approximately 25 vol. %, which agrees with the peak intensities on the diffractometer traces.

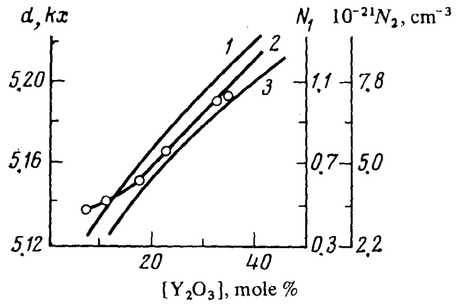

Figure 14. Variation of the lattice constant and of the number of vacancies in a ZrO_2–Y_2O_3 crystal as a function of the Y_2O_3 content: 1) lattice constant d calculated from Eqn. (2); 2) experimental values of d; 3) number of vacancies in the anionic sublattice (N_1—in the unit cell; N_2—in 1 cm^3).

The number of anionic vacancies V per unit cell was determined from the formula $V = 4m/(100+m)$. The plot in Fig. 14*a* shows that each unit cell of the crystal with 33 mole % Y_2O_3 contains one O vacancy, which corresponds to 7.1×10^{21} in 1 cm^3. Fig. 15 presents curves characterising the degree of order in the structure. Evidently the degree of order is a maximum in the presence of 15 mole % Y_2O_3. With decrease of the Y_2O_3 concentration, the degree of order falls sharply owing to the incomplete stabilisation of the cubic structure. With increase of m above 20%, the order in the structure also breaks down owing to the gradual rearrangement of the fluorite type lattice into the lattice of the solid solution of ZrO_2 in Y_2O_3.

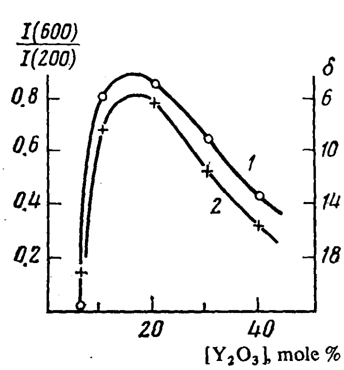

Figure 15. Variation of the degree of order as a function of the Y_2O_3 content: 1) width of (531) line at the level of half its height; 2) ratio of the intensities of the (600) and (200) lines.

Table 4. The densities of zirconium dioxide single crystals as a function of the concentration of the stabilising Y_2O_3 admixture (ρ_1 calculated from X-ray diffraction data and ρ_2 determined by hydrostatic weighing).

$[Y_2O_3]$, mole %	ρ_1, g cm^{-3}	ρ_2, g cm^{-3}	$[Y_2O_3]$, mole %	ρ_1, g cm^{-3}	ρ_2, g cm^{-3}
10.3	5.920	5.910	19.8	5.661	5.655
13.8	5.868	5.863	31.2	5.596	5.603
16.3	5.766	5.800	35.9	5.538	5.543

We calculated the densities of the single crystals from the X-ray diffraction data[39]. These results (ρ_1) together with the experimental values obtained by hydrostatic weighing (ρ_2)[40] are presented in Table 4. The appreciable decrease of the density of the crystals is caused both by the increase of the volume of the unit cell and by the increase of the concentration of the oxygen vacancies. Electron microscope studies, carried out using a "Stereoscan" raster microscope, confirmed that the specimens with 6 mole % Y_2O_3 consist of two phases. The photograph clearly shows inclusions having different structures and orientations. The structure of the crystals with 10–20 mole % Y_2O_3 is homogeneous. The X-ray diffraction data showed that the specimens with 30 mole % Y_2O_3 have a disordered single-phase structure. Nevertheless the electron micrographs showed patterns characteristic of two-phase systems. Presumably a phase having a Y_2O_3 concentration different from the average value, in which the given type of lattice is preserved with somewhat altered parameters, is segregated in these specimens.

Structural Substitutions and Point Defects

The results of the X-ray diffraction analysis and the density measurements showed that the stabilised ZrO_2 and HfO_2 crystals are substitutional solid solutions in which the cations of the stabilising oxide substitute Zr^{IV} ions (atoms). Since we are dealing here with heterovalent substitution, the formation of the solid solution is accompanied by the immediate appearance of several point defects. In terms of structural elements[41], the pattern has the following appearance.

(1) $Zr(Hf)O_2$–AO solid solutions, where A = Mg, Ca, Sr, or Ba. Here the structural elements are as follows: Zr_{Zr}—a zirconium ion in the cationic fluorite sublattice; A_{Zr}—a cation of the stabilising oxide at a site of the zirconium sublattice; V_O—a vacancy at an oxygen subsite of the fluorite sublattice; O_O—an oxygen ion at an anionic lattice site.

The concentrations of the structural elements are related as follows: when the mole fraction of AO in $Zr(Hf)O_2$ is n_1, the fraction of cationic sublattice sites occupied by the A ions is $[A_{Zr}] = n_1$ and the fraction of vacant anionic sublattice sites is $[V_O] = n_1$, which implies that each bivalent ion A introduces one oxygen vacancy.

(2) $Zr(Hf)O_2$–B_2O_3 solid solutions, where B = Sc, Y, La, or Ln. In this case the relative concentrations of the structural elements can be formulated thus: $[B_{Zr}] = 2n_2$; $[V_O] = n_2$; this implies that one oxygen vacancy is introduced by each two tervalent B ions.

Thus stabilisation by the addition of extraneous oxides introduces into the ZrO_2 and HfO_2 crystal lattices a large number of point defects, which greatly influence (as will be shown below) the physical properties of these crystals, particularly the electrical and spectroscopic properties.

Optical Inhomogeneity

The majority of the stabilised ZrO_2 and HfO_2 single crystals which we obtained exhibited a high degree of optical perfection. However, defects were encountered in certain specimens; we shall consider[42] the most typical of these. The optical inhomogeneity of a solid solution is known to be largely determined by the uniformity of the distribution of the solution components, which depends in its turn on the effective partition coefficient. We determined[42] the partition coefficient of Y_2O_3 in the ZrO_2–Y_2O_3 solid solution, and the effective partition coefficient was calculated by the method of Vigdorovich et al.[43] The Y_2O_3 concentration along the length of the crystal was determined by chemical analysis. In the presence of 10 mole% Y_2O_3, the partition coefficient is 1.088.[42]

The study of ZrO_2–Y_2O_3 and HfO_2–Y_2O_3 crystals under the microscope using crossed Nicol prisms revealed a weak inhomogeneity of the extinction caused by internal stresses. The angle between the optical axes was close to 90°. The difference between the refractive indices n_1 and n_2, obtained from the formula $\Delta\lambda = \alpha(n_1 - n_2)$ and a colour nomogram (for a plate thickness $d = 1.5$ mm), was 7.7×10^{-4}. Conoscopic studies showed that isotropic ZrO_2–Y_2O_3 and HfO_2–Y_2O_3 crystals become biaxial and optically positive under the influence of residual stresses, but the degree of deformation is small. The optical indicatrix of the crystals consists of a weakly deformed sphere, slightly extended in the direction of the [011] crystal growth axis. In order to eliminate internal stresses, the crystals were subjected to high-temperature annealing *in vacuo* or in nitrogen. The rate of evaporation of the crystals at different temperatures was determined beforehand and it was found that appreciable evaporation begins at 2100° C. The rates of evaporation at this temperature were $(7-9)\times10^{-6}$ g cm^{-2} s^{-1} for $ZrO_2-Y_2O_3$ and $(3-5)\times10^{-6}$ g cm^{-2} s^{-1} for $HfO_2-Y_2O_3$ (the Y_2O_3 concentration was 10 mole % in both cases). These results showed that it is desirable to carry out the annealing at temperatures not exceeding 2100° C.

The dislocation structure was investigated by the chemical etching method. The most suitable etch is the $2HNO_3 + 3HF$ mixture. The typical density of dislocations in the [111] plane was 5×10^6 cm^{-2}. The etching pits were triangular in shape and were distributed extremely non-uniformly; their density increased markedly at the edges of the single crystal blocks. After annealing, the dislocation density decreased by an order of magnitude.

It has been noted that the crystals become black after annealing *in vacuo* (10^{-3} mmHg) at 2000° C with subsequent rapid cooling (at a rate of 450 K h^{-1}).[42] For low cooling rates, there was no blackening. When the blackened crystals were heated in air at 1200° C, their initial colour and transparency were restored. The blackening is associated with a partial loss of oxygen and the formation of colour centres, the retention of which on rapid cooling is due to the quenching of the reduced state of zirconium. During slow cooling, there is apparently sufficient time for a rearrangement of the lattice and the "reduced" zirconium is reoxidised by atmospheric oxygen.

One of the most characteristic forms of inhomogeneity in the crystals investigated consists of knotlike defects distributed at right angles to the direction of growth. They can be readily seen on shadow-projection patterns recorded by the shining point method[42]. The nature and distribution of the light-scattering particles were investigated using a laser ultramicroscope[42]; the observations were made at an angle of 90° to the direction of the incident beam from the He–Ne laser ($\lambda = 0.63$ μm). In certain $ZrO_2-Y_2O_3$ crystals with an additional admixture of erbium, cerium, and neodymium oxides, microscopic and submicroscopic particles with dimensions ranging from 0.03 to 8 μm were readily seen under the microscope. In highly defective specimens the average density of these particles reached $(0.5-1)\times10^6$ mm^{-3}. Under the influence of prolonged high-temperature vacuum annealing, the scattering particles increase in size and their number diminishes almost by a factor of 2. In $ZrO_2-Y_2O_3$ crystals without an additional admixture light scattering was observed in the form of a Tyndal cone, its intensity depending significantly on the purity of the initial substances and the conditions of crystal growth. Microscope studies showed that in this case the scattering is due to particles with dimensions of the order of 0.1 λ. The Y_2O_3 concentration does not affect the size and number of particles; on the other hand, the addition of a second admixture frequently resulted in the appearance of scattering centres.

Optical Properties

The first measurements of the refractive indices of stabilised ZrO_2 and HfO_2 single crystals were made by Aleksandrov et al.[40] In a later study[42] the refractive indices were measured on a precision goniometer by the prism method; the results of the measurements for $ZrO_2-Y_2O_3$ and $HfO_2-Y_2O_3$ are presented in Table 5, which also illustrates the dependence of the refractive index on the wavelength. It was noted[42] that the refractive index varies along the crystal length, the variation reaching several thousandths, which is due to the non-uniformity of the yttrium oxide concentration.

Table 5. The refractive indices *n* of zirconium dioxide single crystals as a function of yttrium oxide concentration (mole %).

λ, μm	Refractive index *n*			
	$[Y_2O_3]=9$	$[Y_2O_3]=11$	$[Y_2O_3]=15$	$[Y_2O_3]=17$
0.4358	2.2224	2.2101	2.1783	2.1232
0.5461	2.1856	2.1737	2.1434	2.0949
0.5779	2.1790	2.1669	2.1372	2.0897
0.5893	2.1768	2.1653	2.1352	2.0881
0.6328	2.1718	2.1581	2.1287	2.0826

Spectroscopic properties

A characteristic feature of the stabilised ZrO_2 and HfO_2 crystals is a large number of a wide variety of impurities at high concentrations, sometimes reaching 10 mole %. The phase homogeneity of the crystals is unaffected. Lanthanide elements, iron-group elements, chromium, vanadium, titanium, and many others can be introduced into these crystals. Many impurities can exist in several valence states in solid solutions based on ZrO_2 and HfO_2. In essence these solid solutions represent a whole class of substances, which, while retaining their macrostructure and phase homogeneity, can exhibit a variation in their physical properties within wide limits. We shall quote several examples of the spectroscopic properties of solid solutions based on ZrO_2 and HfO_2 with different impurities, illustrating the characteristics of these systems in relation to other impurity-containing crystals used in optics and quantum electronics.

1. Spectra of ZrO_2 and HfO_2 with an admixture of tervalent lanthanides. These crystals are of interest in view of the possibility of their employment in quantum electronics[44–46]. Fig. 16*a* illustrates the combined absorption spectrum of $HfO_2-Y_2O_3-Nd_2O_3$ (0.7 wt.%) at 300 K; Figs. 16*b* and 16*c* illustrate the absorption spectrum of Nd^{3+} ($^4I_{9/2} \rightarrow {}^4F_{3/2}$ transition) and the luminescence spectrum ($^4F_{3/2} \rightarrow {}^4I_{11/2}$ transition) of the same crystal, both recorded at 300 K on a DSF-12 spectrometer. The width of the Stark components of the spectra depends only slightly on temperature and amounts to 100 cm^{-1}. Analogous Nd^{3+} spectra were observed for $ZrO_2-Y_2O_3-Nd_2O_3$ crystals. The measured lifetime of the $Nd^{3+}(^4F_{3/2})$ level was 450 ± 30 μs in both cases. The lasing effect of Nd^{3+} in $ZrO_2-Y_2O_3$ and $HfO_2-Y_2O_3$ was investigated in an elliptical illuminator with an IFP-800 xenon pulse lamp. The resonator consisted of external dielectric mirrors with reflectivities of 99.9 and 97% for $\lambda = 1.06$ μm. A lasing effect was observed for $ZrO_2-Y_2O_3-Nd_2O_3$ crystals at a wavelength of 1.0609 μm and for $HfO_2-Y_2O_3-Nd_2O_3$ crystals at a wavelength of 1.0604 μm. The thresholds of the lasing effects of crystals between 24 and 32 mm long and between 3 and 6 mm in diameter were in the range 7–20 J. The widths of the laser lines were 34 and 38 Å respectively[44]. Thus, in terms of their spectroscopic and laser properties, the crystals of solid solutions based on ZrO_2 and HfO_2 occupy a position intermediate between crystals and glasses, exactly like other crystalline solid solutions

with a disordered structure. It has been noted[47] that the inhomogeneous broadening of the lines in the spectra of lanthanide ions in solid solutions is associated with the number of intrinsic and impurity point defects and increases with increase of the concentration of the impurities introduced.

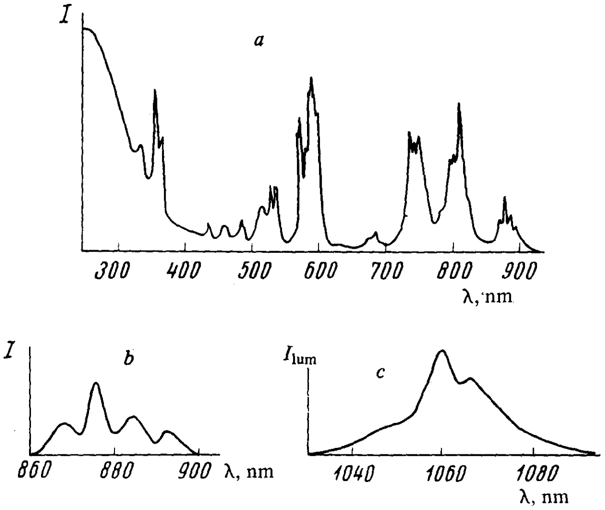

Figure 16. Optical spectra of HfO_2–Nd^{3+} crystals: *a*) absorption spectrum of HfO_2–Y_2O_3–Nd^{3+} (0.7 wt.%) crystals at 300 K: *b*) Nd^{3+} absorption band corresponding to the $^4I_{9/2} \rightarrow {}^4F_{3/2}$ transition; *c*) luminescence spectrum corresponding to the $^4F_{3/2} \rightarrow {}^4I_{11/2}$ transition at 300 K (*I* — line intensity).

The same characteristics of the spectra are typical also for ZrO_2–Er_2O_3–Ho_2O_3 and ZrO_2–Er_2O_3–TmO_3 crystals[46], which are of interest for lasers emitting in the region of wavelengths of approximately 2 μm. Here Er_2O_3 plays simultaneously the role of the stabiliser of the cubic structure and of the sensitiser of holmium and thulium. The lifetimes of the upper working $Ho^{3+}(^5I_7)$ and $Tm^{3+}(^3H_4)$ levels were 6.2 and 1.2 ms at 300 K and 6.6 and 2.5 ms at 77 K respectively. The lifetime of the $^4I_{13/2}$ level of the Er^{3+} ion without Ho^{3+} or Tm^{3+} admixtures was 8.5 ms. In the presence of Ho^{3+} and Tm^{3+} the luminescence of Er^{3+} originating from the $^4I_{13/2}$ level could not be recorded. The lasing effects of ZrO_2–ErO_3 (20 mole %)–Ho_2O_3 (1 mole %) and ZrO_2–Er_2O_3 (20 mole %)–Tm_2O_3 (1 mole %) crystals were observed in an elliptical illuminator with an IFP-2000 xenon pulse lamp. The laser crystals in the form of cylinders 33 mm long and 6.7 mm in diameter were placed in a quartz Dewar vessel with liquid nitrogen. Silver mirrors were deposited on the end-faces of the crystals; the reflection coefficients of the mirrors at the operational wavelengths were 100 and 95%. The lasing effect threshold amounted to 400 J for Ho^{3+} and 420 J for Tm^{3+}; the wavelengths of the lasing effects were 2.115 μm for Ho^{3+} and 1.896 μm for Tm^{3+}, which corresponds to the $^5I_7 \rightarrow {}^5I_8$ and $^3H_4 \rightarrow {}^3H_6$ transitions. For 800 J pumping, a lasing effect appeared in both crystals at $\lambda = 1.620$ μm. The results of the study of these crystals showed that they can find applications in redesigned lasers, since they have much narrower thresholds than glasses for a broad spontaneous emission spectrum.

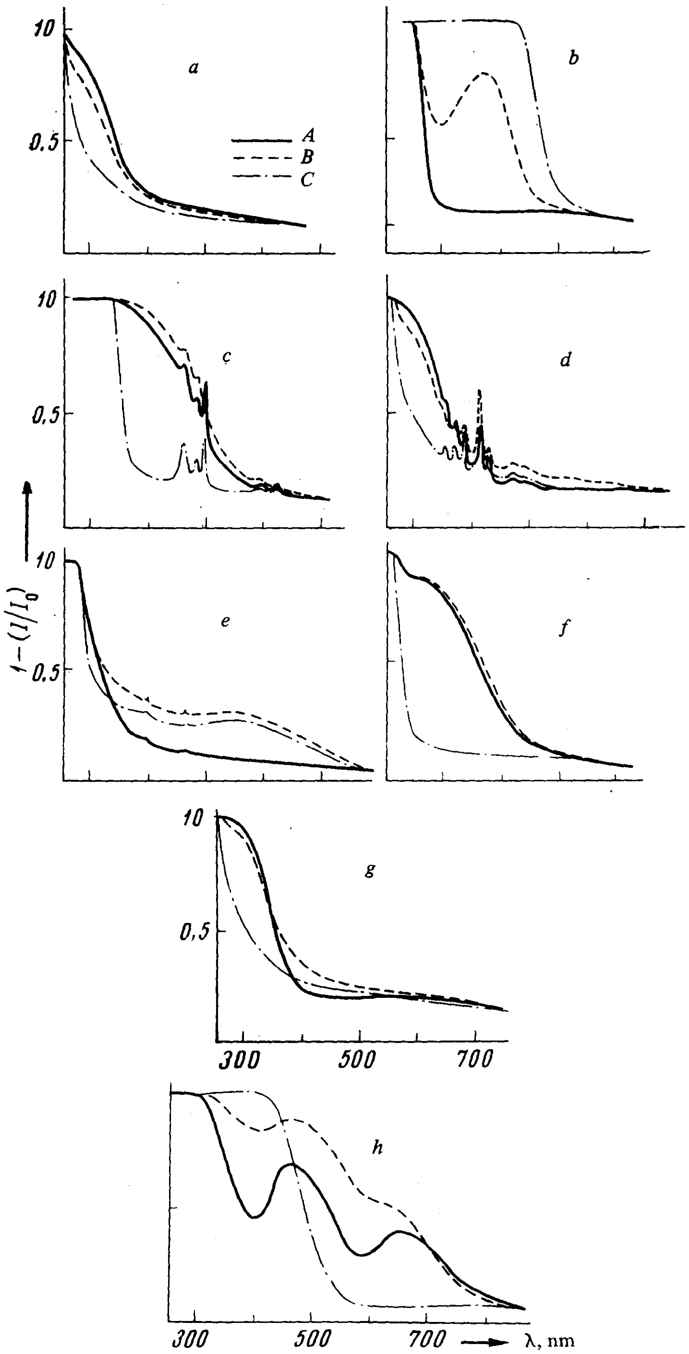

Figure 17. Absorption spectra of ZrO_2–Y_2O_3 crystals grown in air (*A*), after γ-irradiation (*B*), and after vacuum annealing (*C*): *a*) inactivated crystals with $d = 5.47$ mm; crystals activated by the addition of various lanthanides: *b*) Ce, $d = 2.23$ mm; *c*) Pr, $d = 1.90$ mm; *d*) Sm, $d = 0.5$ mm; *e*) Eu, $d = 1.48$ mm; *f*) Tb, $d = 1.61$ mm; *g*) Yb, $d = 4.54$ mm; *h*) Cr, $d = 0.96$ mm.

2. Spectroscopic properties of $Zr(Hf)O_2-Y_2O_3$ crystals with variable-valence impurity ions. In the study of crystals of solid solutions based on ZrO_2 and HfO_2 with impurities it was noted that their optical properties are sensitive to the oxidation-reduction heat treatment conditions and to the effect of ionising radiation. As a rule, these were crystals with admixtures of elements tending to undergo a change in their valence state. These results are of interest not only for spectroscopy but also from the standpoint of the structures of the crystals and the transformations of the structures of point defects. We shall quote data for $ZrO_2-Y_2O_3$ crystals activated by lanthanide and chromium ions[48]. The Ce, Pr, Sm, Eu, Tb, Yb, and Cr concentrations were 0.5 wt.%. The initial substances had the following purities: ZrO_2 was of "specially pure" grade, Y_2O_3 and lanthanide oxides were 99.999% pure, and chromium oxide was of "chemically pure" grade. The absorption spectra were recorded immediately after growing the crystals in air (spectra A) and then after each of the following types of treatment: (1) after exposure to ^{60}Co γ-rays at room temperature up to a dose of 10^7 rad (spectra B); (2) after vacuum annealing at 1800° C (spectra C). The spectra are presented in Fig.17. They evidently vary as a function of the type of treatment of the crystals, the nature of the changes being related to the activator introduced. Only slight changes in the ultraviolet spectrum are observed for the inactivated crystals and crystals with samarium and ytterbium; the changes for the crystals activated with cerium, praseodymium, terbium, europium, or chromium are much more appreciable and they are accompanied by the appearance of new bands or disappearance of old ones in the visible part of the spectrum. The spectrum of the $ZrO_2-Y_2O_3-Ce$ crystal, subjected to additional annealing in an oxidising atmosphere after vacuum annealing, agreed with that of the initial crystal (spectrum A). Heat treatment of γ-irradiated crystals results in the disappearance of bands induced by irradiation; γ-irradiation at 77 K made all the crystals opaque in the visible part of the spectrum. On subsequent heating to room temperature, they were gradually decolorised.

Spectra A

A striking feature of the absorption spectra of the crystals grown in air is the absence of Ce^{3+} bands from the spectrum of $ZrO_2-Y_2O_3-Ce$ and the presence of an absorption band in the region of 3500–6000 K of the spectra of the Pr^{3+} and Tb^{3+} containing crystals together with the absorption bands due to Pr^{3+} and Tb^{3+}. An analogous band in the range 3000–5000 Å appears in the spectra of the γ-irradiated $Y_3Al_5O_{12}-Pr$ and $Y_3Al_5O_{12}-Tb$ crystals, where it is associated with the presence of Pr^{4+} and Tb^{4+} ions[49]. The tervalent Ce^{3+}, Pr^{3+}, and Tb^{3+} ions in the crystals are known to pass readily to the tervalent state[50]. Bearing this feature in mind as well as the oxidising conditions during crystal growth and the favourable conditions for the tetravalent state of the impurity in the ZrO_2 lattice, one may conclude that the entire cerium and part of the praseodymium and terbium are incorporated in the tetravalent state into the crystals of cubic ZrO_2 during the growth process. Under these conditions, admixtures of samarium, europium, ytterbium, and chromium are present as tervalent ions.

Spectra B

γ-Irradiation of crystals containing admixtures of cerium and europium in air leads to the appearance of new bands, compared with spectra A; these are the bands of the Ce^{3+} and Eu^{2+} ions. After irradiation of the crystals containing praseodymium and terbium, the intensity of the band at 3500–6000 Å increases slightly owing to the additional conversion of part of Pr^{3+} and Tb^{3+} into Pr^{4+} and Tb^{4+}. Spectrum B of the crystal with an admixture of chromium does not permit an unambiguous determination of the factor with which the increase of the intensities of the bands present in spectra A is associated. One may assume tentatively that the crystal grown in air contains Cr^{4+} together with Cr^{3+}. The increase of the band intensity can then be attributed to the conversion of Cr^{4+} into Cr^{3+} on γ-irradiation.

Spectra C

It follows from Fig.17 that vacuum annealing has a strong influence on the absorption spectra of the crystals. The band in the range 2600–3700 Å disappears from the spectra of $ZrO_2-Y_2O_3$ crystals and crystals containing samarium and ytterbium; the 3500–6000 Å band disappears from the spectra of crystals with praseodymium and terbium, only the bands characteristic of the lanthanides remaining. By analogy with the $Y_3Al_5O_{12}-Pr$ and $Y_3Al_5O_{12}-Tb$ crystals the absorption band in the region from 3000 Å to the edge of the intrinsic absorption may be identified with the $4f \rightarrow 5d$ transitions in the Pr^{3+} and Tb^{3+} ions. As in spectra B, bands due to Ce^{3+} and Eu^{2+} appear in spectra C of $ZrO_2-Y_2O_3-Ce$ and $ZrO_2-Y_2O_3-Eu$. A new band arises in the region of 4000 Å in the spectrum of the crystal with chromium and the Cr^{3+} bands vanish. All these changes indicate the reduction of activators during vacuum annealing, which is most likely to be associated with the formation of atomic oxygen during this process and its removal from the lattice. Repeated annealing in an oxidising atmosphere restores the original state of the specimens, i.e. the changes occurring on heating the specimens *in vacuo* to 1800° C lead to reversible changes in the nature and concentration of point defects. With increase of the temperature of the vacuum annealing, the changes become irreversible: the crystals blackened *in vacuo* remain turbid after heat treatment in air[42]. The results suggest that the disappearance of the Cr^{3+} bands after vacuum annealing indicates the conversion of Cr^{3+} into Cr^{2+}, while the decrease of the intensity of the 2600–3700 Å band in spectra B and its complete disappearance from spectra C of $ZrO_2-Y_2O_3$, $ZrO_2-Y_2O_3-Sm$, and $ZrO_2-Y_2O_3-Yb$ crystals shows that the band is due to defects having an effective positive charge and containing a captured electron—most probably oxygen vacancies.

Thus the formation of colour centres in the activated crystals of cubic $ZrO_2-Y_2O_3$ solid solutions on γ-irradiation and heat treatment is associated mainly with the capture of charge carriers by activator centres and is determined by their nature. The relatively high radiation stability of $ZrO_2-Y_2O_3$ crystals at room temperature is due to the small depth of the majority of "intrinsic" capture levels in the forbidden gap.

Electrical Properties

It has been established[51] that the ionic type of conductivity predominates in the ZrO_2 ceramics stabilised by CaO, SrO, Y_2O_3, and La_2O_3. Data have been published[52] for the conductivities of polycrystalline zirconium and hafnium dioxide specimens in the temperature range 500–1300° C. Fig. 18 illustrates the temperature dependence of the resistivities of ZrO_2–Y_2O_3 (10 mole %) and HfO_2–Y_2O_3 (10 mole %) single crystals, obtained by the three-probe method[53]. At low temperatures the experimental points lie on curves described by the equation $\rho = 1.6 \times 10^{-4} \exp(1.20/kT)$ for HfO_2–Y_2O_3 (10 mole %) and $\rho = 3.1 \times 10^{-5} \exp(1.12/kT)$ for ZrO_2–Y_2O_3 (10 mole %), where kT is expressed in eV and ρ in Ωcm. The resistivities of various specimens of ZrO_2–Y_2O_3 single crystals having the same nominal compositions differed appreciably in the low temperature region, apparently owing to the different concentrations of defects in the crystals grown under different conditions. If an electric field is applied to a crystal heated to 300° C and above, then a coloured region arises at the negative electrode, which then begins to grow towards the anode. A broad band appears in the absorption spectrum near the intrinsic absorption edge (of the kind obtained after γ-irradiation of the crystals); it can be fairly justifiably assigned to oxygen vacancies which have captured electrons.

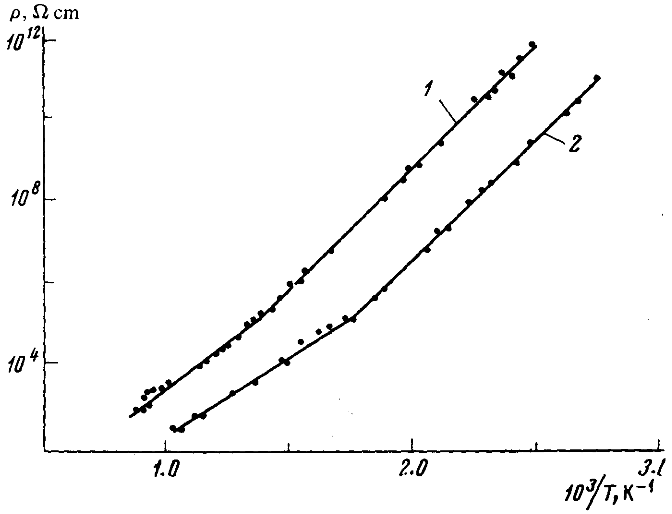

Figure 18. Temperature variation of the resistivity of single crystals: 1) HfO_2–Y_2O_3 (10 mole %); 2) ZrO_2–Y_2O_3 (10 mole %).

Fig. 19 presents the frequency dependence of ϵ tan δ for ZrO_2–Y_2O_3 (10 mole %) and HfO_2–Y_2O_3 (10 mole %), while Fig. 20 shows the temperature dependence of ϵ and tan δ.[53] The relatively small variance of ϵ shows that the polarisation of the crystals investigated has a relaxation mechanism and may be caused by the displacement of weakly bound oxygen vacancies or impurity ions. Fig. 20 shows that ϵ increases with temperature.

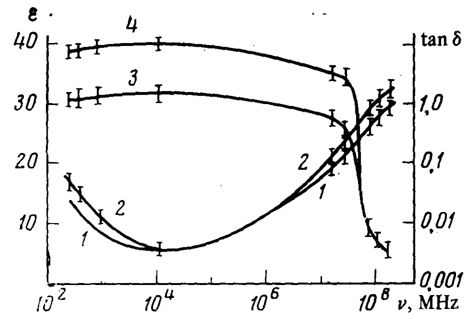

Figure 19. Frequency dependence of ϵ and tan δ for HfO_2–Y_2O_3 (10 mole %) single crystals [1) tan δ; 3) ϵ] and ZrO_2–Y_2O_3 (10 mole %) single crystals [2) tan δ; 4) ϵ].

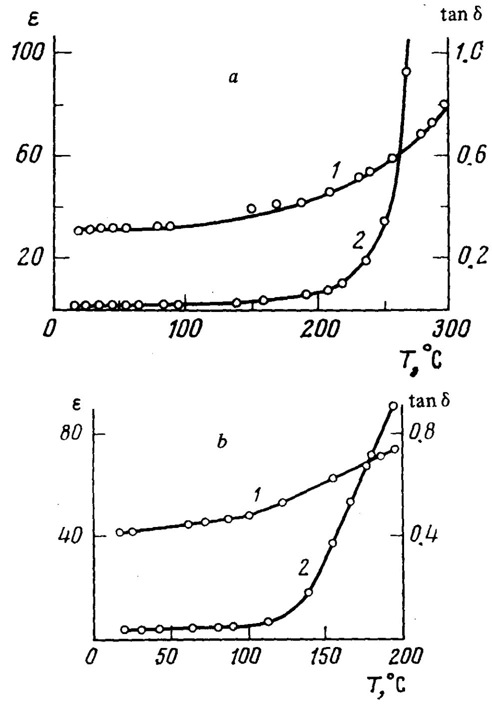

Figure 20. Temperature dependence of ϵ and tan δ for different single crystals: *a*) HfO_2–Y_2O_3 (10 mole %); *b*) ZrO_2–Y_2O_3 (10 mole %); 1) ϵ; 2) tan δ.

The electrical conductivities of zirconium dioxide single crystals have been investigated[54] at temperatures between 800° and 1900° C. The measurements were performed either in a tubular graphite furnace in a vacuum of 0.1 mmHg or in an inert atmosphere by the four-probe method using 50 Hz a.c. on the apparatus already described[55]. The electrical conductivity was measured both with a gradual increase of temperature from 800° to 1900° C and with subsequent stepwise cooling[54]. This made it possible to take into account the influence of the defects associated with the partial reduction of the crystals. Comparison of data for single crystals and ceramic specimens having the same composition showed that the single crystals have a specific conductance greater by a factor of 1.5. Fig. 21 presents data for ternary systems containing 10 mole % of the stabilising impurity and 1 wt.% of one of the lanthanide oxides. Evidently, after the addition of the second admixture, the electrical conductivity increases. It initially rises from cerium to praseodymium and then falls for neodymium and again rises from neodymium to terbium.

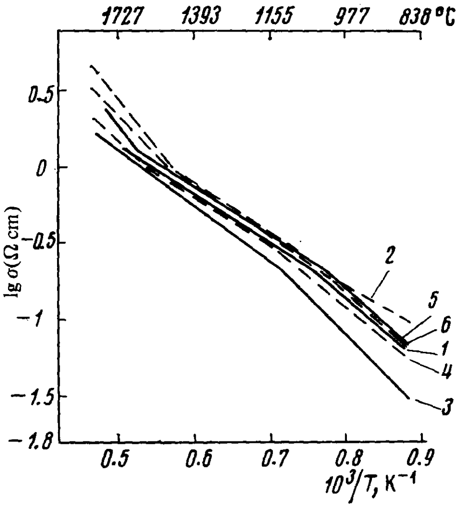

Figure 21. Temperature dependence of the resistivities of single crystals: 1) ZrO_2–Y_2O_3 (10 mole %) + 1 wt.% CeO_2; 2) ZrO_2–Y_2O_3 (10 mole %) + 1 wt.% Pr_6O_{11}; 3) ZrO_2–Y_2O_3 (10 mole %) + 1 wt.% Nd_2O_3; 4) ZrO_2–Y_2O_3 (10 mole %) + 1 wt.% Sm_2O_3; 5) ZrO_2–Y_2O_3 (10 mole %) + 1 wt.% Tb_2O_3; 6) ZrO_2–Y_2O_3 (10 mole %) + 1 wt.% Yb_2O_3.

Elastic, Photoelastic, and Acoustic Parameters

The elastic, photoelastic, and acoustic properties of ZrO_2–Y_2O_3 and HfO_2–Y_2O_3 single crystals have been measured[56–58] by the method of Mandelstam–Brillouin light scattering. The studies were performed on the experimental apparatus already described[59]. An Ar^+ laser served as the source of light at a wavelength of 5145 Å. The scattered light spectrum was investigated with the aid of a Fabry–Perot étalon, scanned as a function of pressure, and was recorded photoelectrically using a photon counting technique. The results of the data interpretation are presented in Tables 6–8. Analysis of the results led to the following findings:

1. In ZrO_2–Y_2O_3 and HfO_2–Y_2O_3 solid solutions there are directions of excited and scattered light for which longitudinal waves hardly contribute to light scattering. Analogous results had been obtained previously for non-cubic sapphire[61] and lithium niobate crystals[62].

2. The velocities of the longitudinal and transverse sound waves in ZrO_2–Y_2O_3 solid solutions depend significantly on the direction of their propagation, i.e. these cubic single crystals are strongly anisotropic with respect to the velocity of sound.

3. The constants C_{11} and C_{44} vary monotonically with the Y_2O_3 concentration, while C_{12} varies non-monotonically.

4. The elastic anisotropy of ZrO_2–Y_2O_3 crystals is very considerable and varies from 2 to 2.6 depending on the Y_2O_3 content. It follows from Table 7 that the photoelastic anisotropy of these crystals is just as great. It increases from 1.80 to 2.85 with increasing Y_2O_3 concentration.

Table 6. Acoustic parameters of ZrO_2–Y_2O_3 single crystals.

$[Y_2O_3]$, mole %	ρ, g cm^{-3}	Direction of propagation of sound	Polarisation of sound	Velocity of sound, km s^{-1}		Elastic constants × 10^{12}, dyn cm^{-2}			Debye temp., K
				Ref.57	Ref.60	C_{11}	C_{44}	C_{12}	
8	5.99	[110[	[001]	—	3.05	—	—	—	—
		[110]	$[1\bar{1}0]$	—	5.02	3.94	0.56	0.91	543
		[110]	[110]	—	7.05	—	—	—	—
10.3	5.91	[100]	[001]	3.12	—	—	—	—	—
		[100]	[100]	8.26	—	—	—	—	—
		$[1/2-1/2,\ \sqrt{1/2}]$	T_1	4.54	—	4.03	0 58	0.83	555
		$[1/2-1/2,\ \sqrt{1/2}]$	T_2	—	—	—	—	—	—
		$[1/2-1/2,\ \sqrt{1/2}]$	L	6.89	—	—	—	—	—
12	5.89	[110]	[001]	—	3.24	—	—	—	—
		[110]	$[1\bar{1}0]$	—	5.78	4.49	0.62	0.55	584
		[110]	[110]	—	7.30	—	—	—	—

Table 7. Elastic and photoelastic properties of ZrO_2–Y_2O_3 single crystals.

$[Y_2O_3]$, mole %	ρ, g cm^{-3}	Elastic anisotropy $(C_{11}-C_{12})/2C_{44}$	n	Photoelastic constants*			Anisotropy $(P_{11}-P_{12})/2P_4$
				P_{11}	P_{12}	P_{44}^*	
10	5.95	2.401	2.193	—	—	—	1.80
12	5.89	2.559	2.183	0.285	−0.115	0.100	2.00
16.5	5.81	2.347	2.177	—	—	—	2.63
20	5.76	2.001	2 174	0.470	−0.101	0.100	2.85

* It was arbitrarily assumed that the constant P_{44} = 0.100.

By virtue of a unique combination of their physical and physicochemical properties, fianit single crystals may be used in optics, high-temperature engineering, quantum electronics, and in the manufacture of jewellery. Fig. 22 presents photographs of technical articles (lenses, prisms, windows, crucibles, laser elements, and electrodes) made of fianits.

VI. PREPARATION OF HIGH-TEMPERATURE GLASSES

The glasses are usually prepared in gas or electrical furnaces in platinum or ceramic crucibles[63]. The same problems then arise as in the growing of crystals from the melt: (1) the difficulty of obtaining a product uncontaminated by the material of the crucible and (2) the difficulty of obtaining glasses at temperatures above 1600–1700° C. The first experiments on the preparation of glasses in a cold container were described by Aleksandrov et al.[14] and a later report[64] dealt with the preparation of glasses in quartz beakers exposed to a stream of gas with direct heating of the glass mass by high-frequency currents.

Certain properties of new high-temperature R_2O_3–Al_2O_3–SiO_2 glasses, where R_2O_3 = scandium, yttrium, or lanthanum oxide or the oxide of another lanthanide, are described below[65]. The preparation of glasses in a cold container has characteristic features distinguishing it from the preparation of crystals. In the first place the glasses do not have a distinct melting point and there is therefore also no distinct interface between the melt and the solid phase. The transition from the solid substance adjoining the walls of the cold container to the melt is gradual via a vitreous substance with a gradually diminishing viscosity. Another characteristic feature is the high viscosity of the glass melt, which hinders convection, mixing of the components, the removal of the glasses, and ultimately the homogenisation of the melt and the formation of a glass of a high optical quality. Fig. 23 presents a scheme for the preparation of high-temperature optically homogeneous glasses. We used a cooled stirrer in order to agitate the viscous melt. A crust of solid glass grows on the part of the stirrer immersed in the melt, so that stirring does not result in the contamination of the material.

Table 8. Velocity of sound in HfO_2–Y_2O_3 (10 mole %) {direction of exciting light [110]}.

Direction of scattered light	Wave*	Velocity of sound, km s^{-1}
$[\bar{1}10]$	L	6.29±0.04
$[\bar{1}10]$	T_2	2.50±0.02
[001]	qL	5.46±0.02
[001]	T_2	3.20±0.01
[001]	qT_1	3.48±0.04

*Notation: L = longitudinal sound wave; T_2 = transverse sound wave with the direction of polarisation at right angles to the scattering plane; T_1 = ditto with the direction parallel to the scattering plane. The prefix q indicates that the sound wave is quasi-longitudinal or quasi-transverse.

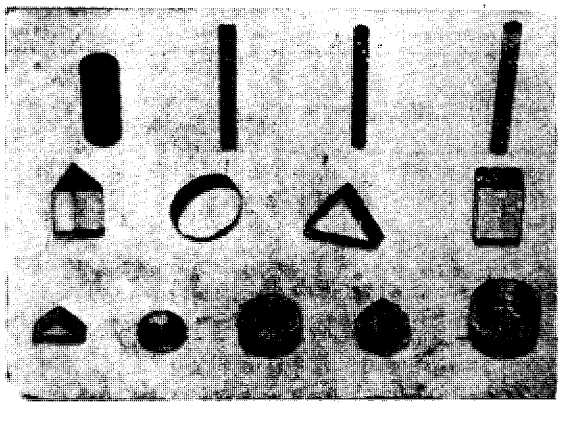

Figure 22. Photograph of technical articles made of fianits.

The glass was prepared over a period of several hours. The melt in the container was then cooled to 800° C and the resulting block was removed from the container and transferred to a Silit furnace for annealing (at 800° C), which was continued for 8 h. In order to obtain specimens of specified shape, the glass melt was poured into graphite boats. Glass blocks weighing up to 1.5 kg each were thus prepared. The glasses were optically homogeneous and did not contain bubbles or sections which had not been fused. Small bubbles were present only in a narrow region of the viscous melt adjoining the walls of the container.

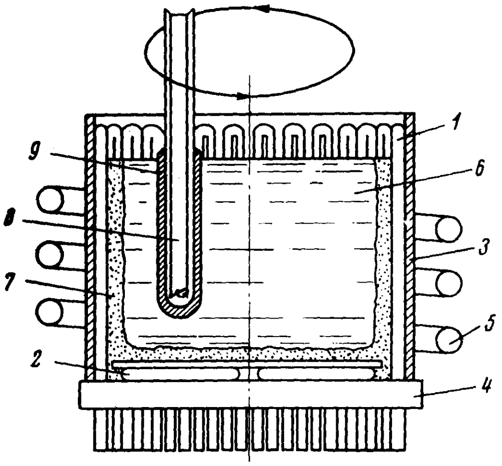

Figure 23. Scheme for the preparation of high-temperature glasses in a cold container: 1) tubular water-cooled element; 2) water-cooled bottom; 3) insulating quartz cylinder; 4) retaining ring of electrically insulating material; 5) inductor of high-frequency generator; 6) melt; 7) charge; 8) water-cooled stirrer; 9) garnissage.

Physicochemical Properties

The softening temperature of the metasilicate section through the Y_2O_3–Al_2O_3–SiO_2 system is in the range 1100–1300° C and increases with decrease of the Y_2O_3 concentration[65]. Analogous data were obtained also for scandium, lanthanum, and erbium glasses. The nature of the dilatometric curves for glasses with small amounts of added R_2O_3 is of interest (2–10 wt.%). Up to 1000° C normal thermal expansion of the glasses is observed, at 1000–1050° C the specimens undergo a sharp contraction, which terminates just as abruptly on further increase of temperature, and softening begins only above 1300° C (Fig. 24). An exothermic effect on the differential thermograms corresponds to the termination of the primary contraction (at 1000–1050° C) and an endothermic effect corresponds to the onset of softening. The exothermic peak is higher the smaller the content of the oxide R_2O_3. This effect is associated with the crystallisation of the glass. X-Ray and micro-X-ray spectroscopic studies on the specimens showed that, when glasses with small amounts of added R_2O_3 crystallise, the mullite phase ($3Al_2O_3.2SiO_2$) is produced. With increase of the R_2O_3 content, crystals of tervalent metal silicates or aluminosilicates begin to be formed. Glasses containing Sc_2O_3 and La_2O_3 exhibit the highest and lowest capacities for crystallisation respectively, which is due to the difference between the basic properties of the oxides.

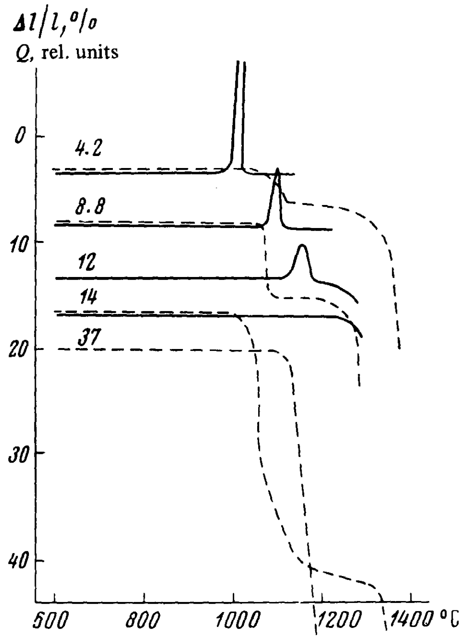

Figure 24. Dilatometric curves (shown dashed) and differential thermograms (shown continuous) for Er_2O_3–Al_2O_3–SiO_2 glasses (the numbers against the curves represent molar percentages of Er_2O_3). The origins of coordinates for the $\Delta l/l$ curve have been displaced along the ordinates axis relative to the upper curve.

Physicochemical and Electrical Properties

Table 9 presents the properties of certain high-temperature glasses obtained in a cold container[65]; the corresponding properties of quartz glass are included for comparison[66]. Evidently the mechanical properties of the glasses are similar to or somewhat superior to those of fused quartz, the softening temperatures of the glasses approaching that of quartz, while their refractive indices are higher than that of quartz. In contrast to the quartz glass, it is easy to introduce various admixtures, including lanthanides, into the glasses.

VII. THE PREPARATION AND PROPERTIES OF FUSED POLYCRYSTALLINE CERAMIC MATERIALS

The preparation of fused polycrystalline materials, used to make cast or pressed ceramic articles, differs little in principle from the process described above, which occurs in the course of high-temperature chemical reactions or when the crystals and glasses are synthesised. The melt having the required composition, prepared by the method described above, is kept for some time in the superheated state for homogenisation and then cooled rapidly. This results in the mass crystallisation of the melt and the latter sets in its entirety into a polycrystalline ingot consisting of fairly large crystalline grains. The fusion is usually carried out in containers having the design illustrated in Fig. 6*a*. Containers shown in Fig. 6*c* are used for the continuous fusion of the polycrystalline ingot.

Table 9. Physicomechanical and electrical properties of high-temperature glasses.

Property	Composition of glass, wt.%				
	quartz glass	$SiO_2:Al_2O_3:Sc_2O_3=60:30:10$	$SiO_2:Al_2O_3:Y_2O_3=50:20:30$	$SiO_2:Al_2O_3:La_2O_3=54:21:25$	$SiO_2:Al_2O_3:Er_2O_3=60:30:10$
Density, g cm^{-3}	2.20—2.21	2.578	3.05	3.016	2.833
Refractive index	1.4588	1.542	1.592	1.573	1.555
Young's modulus, kg mm^{-2}	7450—7140	12 740	11 040	9650	9080
Shear modulus, kg mm^{-2}	3200	5 100	4510	3940	3660
Poisson coefficient	0.16	0.249	0.225	0.225	0.240
Microhardness, kg mm^{-2}	795	780	1050	735	930
Coefficient of linear expansion, K^{-1}	$5\div7\cdot10^{-7}$	$27\cdot10^{-7}$	$70\cdot10^{-7}$	$28\cdot10^{-7}$	$10.3\cdot10^{-7}$
Temperature of onset of softening, °C	1250	1200—1250	1000	1100—1200	1150—1200
Resistivity, Ω cm					
at 20°C	$1\cdot10^{19}$—$1\cdot10^{18}$	$3\cdot10^{13}$	$2\cdot10^{13}$	$4\cdot10^{13}$	$1\cdot10^{13}$
at 600°C	$6\cdot10^{7}$—$6\cdot10^{6}$	$1.7\cdot10^{5}$	—	$1\cdot10^{5}$	$1.7\cdot10^{7}$
at 1000°C	$1\cdot10^{6}$—$2.5\cdot10^{5}$	$1.1\cdot10^{4}$	—	$5\cdot10^{3}$	$5\cdot10^{3}$
Dielectric constant at 20°C	3.2	6.8	7.0	7.1	6.9
Tangent of the dielectric loss angle in the frequency range 30 kHz-10 MHz	$2\cdot10^{-4}$	$5\cdot10^{-4}$	$2\cdot10^{-4}$	$1\cdot10^{-4}$	$2\cdot10^{-4}$

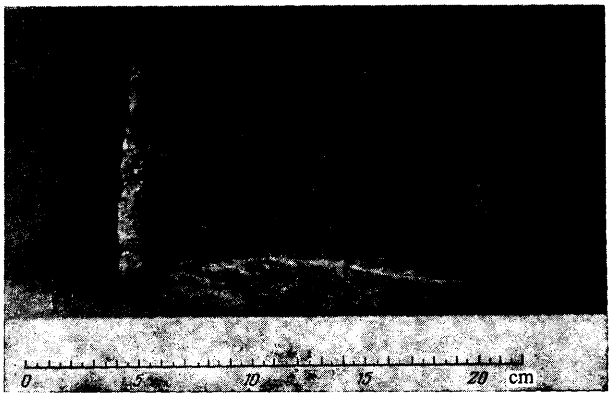

Figure 25. Photograph of a polycrystalline yttrium oxide ingot.

As an example, Fig. 25 presents a photograph of an yttrium oxide ingot. Its structure, indicating the form of the crystallisation isotherm, is clearly seen. We are in essence dealing here with directed crystallisation, since, even after the instantaneous switching off of the high-frequency generator, the large mass of the melt cools non-uniformly (faster at the water-cooled walls than in the centre), as a result of which a temperature gradient is established in the bulk of the melt. Furthermore, a very large number of crystal nuclei, on which crystallisation takes place, are present at the walls of the solid shell. There are no nuclei in the central part of the melt and the onset of nucleation and crystal growth requires some supercooling. Nevertheless, even under these temperature conditions, some materials crystallise in the bulk phase, simultaneously in all parts of the melt. Yttrium chromite and yttrium aluminium garnet melts crystallise in this way (in air). As a result, ingots of these materials do not consist of large elongated blocks but comprise small isometric crystals. The nature of the crystallisation of the melt (directed or bulk phase) determines the homogeneity of the chemical and phase compositions of the ingot. This applies particularly to incongruent crystallisation and especially to the crystallisation of melts having a complex composition.

Figure 26. Electron micrograph of an $LaCrO_3$ ingot to which 7 mole % of calcium chromite has been added.

The Preparation and Properties of Electrically Conducting Fused Oxide Ceramic Materials

Oxide ceramic materials exhibiting ionic or electronic conduction have recently become important in connection with the development of high-temperature technology. Among the technical problems requiring the use of such materials, mention may be made of the formation of heating elements for furnaces giving temperatures up to 2000° C in an oxidising medium, the formation of the electrode walls of magnetohydrodynamic generators, and the development of sensors of the composition of the atmosphere at high temperatures. The manufacture of ceramic partitions with ionic conduction for new chemical current sources also represents an important problem. A new type of conducting material—lanthanum and lanthanide chromites having the general formula $RCrO_3$ and containing an admixture of calcium chromite—was proposed in 1960.[67] Later these materials were investigated[68-71] and it was found that they exhibit electronic conduction, the conductivity being fairly high even at room temperature.

A method has been developed for the synthesis and crystallisation of scandium, yttrium, lanthanum, and lanthanide chromites from the melt in a cold container[13,15]. The chromites obtained from the melt have a well-formed crystal structure and a high chemical purity and phase homogeneity. Certain properties of the fused chromites and the ceramics based on them are given below. Fig. 26 presents electron micrographs of the cleavage plane of the $LaCrO_3$ ingot containing an admixture of 7% of calcium chromite. The photographs clearly show crystalline grains of the lanthanum–calcium chromite solid solution and drops of the eutectic composition enriched (as shown by the X-ray microspectroscopic analysis) in calcium oxide, displaced to the boundaries between the crystals. The chromite ingots were ground and ceramic articles were made from the resulting powder by various procedures of ceramic technology.

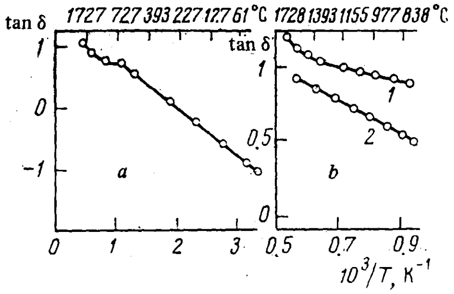

Figure 27. Temperature dependence of the electrical conductivity of a lanthanum chromite specimen to which 7 mole % of calcium chromite has been added: *a*) directly after preparation; *b*) heating in air (curve *1*) and cooling in argon (curve *2*).

Fig. 27 illustrates the temperature variation of the specific conductance of the ceramic made from fused lanthanum chromite with an admixture of calcium†. This material exhibits a high electrical conductivity even at room temperature. An interesting feature of the chromite ceramic is the marked dependence of its electrical conductivity on the oxidation-reduction properties of the atmosphere. A high conductivity in the temperature range between room temperature and 1000° C is ensured only after heat treatment of the specimens in an oxidising atmosphere. Heat treatment in a reducing or a neutral atmosphere or *in vacuo* sharply increases the resistivity of the ceramic in the low-temperature region (Fig. 27). Reheating in an oxidising atmosphere fully restores the initial conductivity. X-Ray diffraction studies on melted lanthanum chromite showed that the material subjected to reductive annealing contains only one phase ($LaCrO_3$). After heat treatment in an oxidising medium, the X-ray diffraction patterns show, together with the lines of the above phase, new lines indicating the appearance of an admixture of a new phase. Thus one may conclude that the electronic conductivity below 1000° C is associated with the formation in the material of admixtures in which the valence of chromium is higher than 3. The melted chromites obtained readily

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†The conductivity data for the lanthanum and yttrium chromite ceramics were obtained by E.G.Spiridonov and V.G.Gordon at the High Temperature Institute (IVTAN).

combine with other metallic and non-metallic phases, initiating a new series of multiphase materials.

One of the most attractive ceramic materials for the manufacture of components with ionic low-temperature conduction for new current sources is Na-β-alumina having the composition $Na_2O.11Al_2O_3$.[72,73] By virtue of the characteristic features of the crystal structure of this compound, Na^+ ions are highly mobile even at 300° C, which makes it possible to employ the Na-β-alumina ceramic for partitions in sodium–sulphur accumulators. This compound is usually synthesised by sintering the initial components (Na_2CO_3 and Al_2O_3) below the melting point (m.p. 1930° C)[73,74]. It is then difficult to drive the reaction to completion and to ensure the absence of admixtures of non-conducting phases which increase the electrical resistivity of the product. Na-β-alumina has been synthesised and crystallised in the melt using the technique of direct high-frequency fusion in a cold container[74]. The starting materials were Al_2O_3 and Na_2CO_3 with a high degree of purity. The components were mixed and heat-treated for 2 h at 1000° C in order to remove the bulk of CO_2. After this the mixture, which had partly interacted, was transferred to a cold container and fused. The starting metal was aluminium. After the fusion of the material, the melt was maintained for 10–20 min at ~ 1980° C, whereupon the components reacted fully and the melt was homogenised. The power supplied to the melt was then gradually reduced and crystallisation was carried out. Single crystals grew on the surface of the melt in the form of square planar plates, the size of the sides of which reached up to 20 mm. The entire ingot was found to consist of fine crystalline blocks. The ingots were ground and ceramic articles were made from the powder. The densities of the specimens obtained were in the range 3.17–3.19 g cm^{-3} and the resistivities, measured using 150 kHz a.c. at 300° C, were 3–10 Ω cm.

If impurities are introduced to synthesise electrically conducting materials (we have in mind non-metals), then the electrically insulating materials must exhibit a high degree of chemical purity and structural perfection. In this respect the technique under consideration has many possibilities. A number of high-temperature insulating materials have been obtained: calcium and strontium zirconates and hafnates and yttrium, scandium, etc. oxides[15]. They all exhibit a high chemical purity, phase homogeneity, structural perfection and as a result have effective electrically insulating properties up to 2000° C. Owing to their high melting points, it is difficult to obtain these materials with a high purity, excluding the possibility of impurity conductivity, by other methods.

Another class of substances with interesting "electrical" properties, which are successfully obtained by crystallisation in a cold container, are dielectrics of the type of lanthanide titanates and zirconates (Table 3).[75]

The Preparation and Properties of Fused Materials for Refractory Ceramics

Refractory polycrystalline ceramics are widely used in metallurgy, chemistry, and high-temperature technology. The main requirements which must be met by such ceramics is high thermal stability and chemical stability at high temperatures. Both these properties are closely related to the chemical purity and structural perfection of the material of the ceramic. The use of the method of direct high-frequency fusion in a cold container[15] led to the preparation of fused polycrystalline ingots of many refractory materials: mullite, yttrium, scandium, and certain lanthanide oxides, spinels, zirconates, ternary aluminium, zirconium, and silicon oxide compounds (bakor) and certain silicates (Tables 2 and 3). Several examples are given below.

1. Mullite[76-78]. By virtue of its excellent thermal stability, this compound, which melts at 1910° C, is one of the most effective refractory materials. It is usually synthesised by the method of solid-phase reactions, which is time consuming and yields a product contaminated by the phases of the unreacted components. The mullite ingot obtained by crystallising the melt in a cold container consists of long prismatic needles oriented in the direction of crystallisation of the ingot. Analysis of the ingots showed that the crystalline phase in any part of the ingot has a composition differing from that of the individual compounds $3Al_2O_3.2SiO_2$ and $2Al_2O_3.SiO_2$ and corresponds to an intermediate composition in the region of a continuous series of solid solutions[76,77]. Table 10 presents certain properties of the ceramics obtained from fused mullite.

Table 10. The properties of ceramics based on materials obtained by direct high-frequency fusion in a cold container.

Property	Composition				
	$3Al_2O_3\cdot 2SiO_2$	Sc_2O_3	Y_2O_3	Gd_2O_3	Er_2O_3
Purity, %	99.7	99.0	99.9	99.98	99.9
M.p., °C	1970	2405	2410	2330	2340
True density, g cm^{-3}	3.15	3.96	5.03	8.33	8.66
Apparent density, g cm^{-3}	2.5—2.6	3.28	4.25	6.8	7.5
Apparent porosity, %	17—18	15—19	14.8	18.4	15.5
Ultimate compressive strength, kg cm^{-2}	500	1400	190	300—350	300—350
Ultimate bending strength, kg cm^{-2}					
at 20°C	150	—	120	—	—
at 1000°C	—	—	100	100—200	100—200
at 1300°C	—	—	125	—	—
at 1400°C	—	—	—	20	20
Modulus of elasticity $10^6 E$, kg cm^{-1}	0.37	—	1.5	—	—
Temperature of deformation under 2 kg cm^{-2} load, °C					
onset of softening	1760—1810	—	1950	—	—
4% contraction	1780—1830	—	2250	1700—1800	1700—1800
Creep *in vacuo*, mm mm^{-1} h^{-1}	—	—	—	—	—
at 1650°C, 14.7 kg cm^{-2} load	—	—	$9.8\cdot10^{-4}$	—	—
Coefficient of linear expansion, K^{-1}					
at 20–800°C	—	—	$7.3\cdot10^{-6}$	$8.4\cdot10^{-6}$	$7.5\cdot10^{-6}$
at 850°C	$4.4\cdot10^{-6}$	—	—	—	—
Resistivity, Ω cm					
in vacuo at 1000°C	—	—	$2.5\cdot10^{6}$	—	—
in vacuo at 1500°C	—	—	$3.0\cdot10^{3}$	—	—
in air at 1000°C	—	—	$1\cdot10^{6}$	10^4—10^5	—
in air at 1600°C	—	—	$3\cdot10^{3}$	—	—
Thermal conductivity at 1200°C, kcal m^{-1} h^{-1} K^{-1}	—	—	0.75	—	—
Thermal stability at 1300°C in water	—	—	12	—	—
Rate of evaporation *in vacuo*, g cm^{-2} s^{-1}					
at 1700°C	$0.5\cdot10^{-7}$	—	—	—	—
at 1800°C	$1.0\cdot10^{-7}$	—	—	—	—
at 1900 °C	—	—	$1.6\cdot10^{-8}$	$6.0\cdot10^{-5}$	$1.2\cdot10^{-5}$
at 2000°C	—	—	$1.5\cdot10^{-7}$	$2.0\cdot10^{-4}$	$1.9\cdot10^{-5}$

2. Y_2O_3, Gd_2O_3, Er_2O_3, and Sc_2O_3.[79-83] The dense polycrystalline yttrium oxide ceramic is highly refractory, has effective dielectric and mechanical properties, and is involatile. We used yttrium oxide of type Y–O with an overall impurity content of ~ 0.1% for fusion

and crystallisation[82]. The fusion process was initiated with metallic yttrium having the corresponding purity. In order to obtain an ingot consisting of large crystals, after heat treatment for 15–20 min the container with the melt was lowered at a rate of 100–200 mm h^{-1} relative to the inductor, which resulted in directed crystallisation of the melt. The ingot obtained was colourless on the outside, but after cleavage it was seen that its internal regions were intensely coloured greyish-blue. After annealing in air at 1200° C, the colour disappeared. These findings showed that, even on fusion in air, yttrium oxide is partly reduced, which leads to the formation of colour centres. As the outer parts of the material in contact with the oxidising atmosphere are cooled, the previously reduced yttrium is reoxidised to the tervalent state. Fig. 25 presents a photograph of an yttrium oxide ingot consisting of large crystals. A granular ceramic material was obtained from fused Y_2O_3 by pressing using a liquid binder; some of its properties are presented in Table 10.

Fused polycrystalline gadolinium, erbium, and scandium oxides are extremely promising as high-temperature constructional materials. The preparation of these substances does not differ in principle from the preparation of crystalline yttrium oxide. Some of the properties of the granular ceramics obtained from fused Sc_2O_3, Gd_2O_3, and Er_2O_3 [81-83] are presented in Table 10.

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Examination of the possibilities of the new technology and the study of the properties of the materials obtained with its aid permit the following conclusions.

Direct high-frequency fusion in a cold container has major technological advantages. For example, it is possible to obtain with the aid of this technique multiphase eutectic compositions and structured compound materials of the metal–oxide and oxide–oxide types by direct fusion and crystallisation of the melt in a cold container as well as new glasses, single crystals, and single-phase ceramic materials, some of which were described above.

By virtue of its fundamental advantages and the ease of its practical application, the method described above constitutes a satisfactory basis for the creation of an effective industrial technology for the preparation of a large class of high-temperature non-metallic materials on which progress in many modern branches of engineering and industry depends significantly.

The method has also many possibilities for scientific research at high temperatures: in the study of chemical reactions in the melt, heterophase equilibria, the physical and physicochemical properties of melts, etc., and also for studies on the chemistry of high-temperature materials.

Not only the final products but also fused half-finished articles for use in the growing of sapphire, garnet, etc. single crystals and in glassmaking by traditional methods can be obtained by means of the technology involving fusion in a cold container.

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Radiation Effects in the Chemistry of Group IVB Elements (Silicon, Germanium, Tin, and Lead)

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Data concerning the effect of ionising radiation on the principal reactions in organometallic synthesis involving Group IVB elements are considered: radiolysis of organometallic compounds of Group IVB elements, addition to the C=C bond, redistribution of radicals, reactions leading to the substitution of functional groups or organic substituents at the metal atom, reactions involving the organic group, and direct synthesis of organometallic compounds from the metal and alkyl halides.
The bibliography includes 104 references.

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I. INTRODUCTION

Physical methods for the stimulation of chemical processes have been acquiring increasing importance in synthetic chemistry. Together with methods whose application dates back to the XIXth century (electrochemistry and photochemistry), various types of radiation (laser, ultrahigh-frequency, and γ-radiation) have found fairly extensive applications during recent decades[1].

This review is devoted to the experience gained in the use of γ-radiation in reactions of Group IVB elements. There are many reviews in the literature demonstrating the wide scope of the application of ionising radiation in organic synthesis; however, the reactions of Group IVB elements have been described fragmentarily (for example, direct synthesis has been described for tin and hydrometallation for silicon)[2-13]. The influence of ionising radiation on reactions of Group IVB elements has not been considered systematically, although extensive data have accumulated in the literature on this problem.

II. RADIATION STABILITY OF COMPOUNDS CONTAINING SILICON, GERMANIUM, TIN, AND LEAD ATOMS

In the study of the influence of radiation on chemical reactions the main task was to discover whether radiation-chemical synthesis is possible. From the standpoint of the utilisation of substances in radiation-chemical synthesis, data on radiation stability and pathways leading to the decomposition of molecules under the influence of high-energy radiation are very important.

Brinskman et al.[14] investigated the mode of dissociation of chemical bonds in organometallic compounds of Group IVB elements and showed (by ESR) that for low energies the decomposition involves mainly the M-C bond, while for high energies the situation becomes more complicated.

It was found for trichloromethylgermane at −196° C that the primary radiolysis products are the $CH_3^{\cdot}$ and $GeCl_3^{\cdot}$ radicals, which enter into secondary reactions via two pathways:

$$CH_3GeCl_3 \xrightarrow{h\nu} CH_3^{\cdot} + GeCl_3^{\cdot},$$

$$\begin{array}{l} GeCl_3^{\cdot} + CH_3GeCl_3 \xrightarrow{1} HGeCl_3 + Cl_3GeCH_2^{\cdot} \\ \qquad\qquad\qquad\quad \xrightarrow{2} GeCl_4 + CH_3GeCl_2^{\cdot} \end{array} .$$

The secondary processes proceed mainly via pathway 2.

The decomposition of silicon compounds under the influence of temperature and an electron beam has been most widely investigated (in connection with the development of the method for the preparation of semiconducting silicon films)[15,16]. The decomposition is usually carried out in the gas phase at elevated temperatures (150-200° C) and electron energies in the range 250-800 eV. (We may note that the thermal decomposition of organosilicon compounds begins above 500° C.) A study of the decomposition of triethylvinylsilane under the influence of an electron beam showed that the rate and mode of decomposition of organosilicon compounds depend less on electron energy and more on the temperature of the support and the vapour pressure of the organosilicon compound. Below 100° C and at a high vapour pressure, polymers are formed, while at higher temperatures elemental silicon is produced[17]. The radiolysis of tetrasubstituted organosilicon compounds proceeds in different ways depending on the phase state of the substance. The gas-phase radiolysis of tetramethylsilane leads ultimately to a complex mixture of products[18,19]: H_2 ($G = 8.56$), C_2H_6 ($G = 4.23$), CH_4 ($G = 1.28$), $C_2H_5Si(CH_3)_3$ ($G = 4.52$), and $(CH_3)_6Si_2$ ($G = 1.4$), where G is the radiation-chemical yield (mol./100 eV). A more detailed study of the mechanism of the radiolysis using the O_2 and NO radical trapping agents established that the majority of the products are formed as a result of secondary processes. The primary stages in the radiolysis are reactions involving the elimination of a hydrogen atom from the organic group:

$$(CH_3)_4Si \rightsquigarrow (CH_3)_3SiCH_2^{\cdot} + H^{\cdot}$$

or the elimination of the methyl radical

$$(CH_3)_4Si \rightsquigarrow (CH_3)_3Si^+ + CH_3^{\cdot} + e^- \quad .$$

Hydrogen and methane are formed as a result of atomic reactions and molecular elimination reactions, while ethane is produced as a result of the recombination of methyl radicals.

The study of the radiolysis of tetramethylsilane by ESR[20] in the solid phase permitted certain comparisons between hydrocarbons and organosilicon compounds. It was shown that the yield of free radicals in alkyl- and aryl-substituted organosilicon compounds hardly differs from that observed in hydrocarbons ($G \simeq 5$), which is consistent with the comparable Si–C and C–C bond dissociation energies. The ESR spectra of irradiated (77 K) alkylchlorsilanes[2] indicate the dissociation of the C–H, Si–C, and Si–Cl bonds, while free radicals are formed from the corresponding carbon compounds mainly as a result of the dissociation of the C–Cl bond. The yield of radicals in the radiolysis of unsaturated organosilicon compounds has been determined[22].

In contrast to the gas phase[18], the radiolysis of tetramethylsilane in the liquid phase[23] is characterised by an increase of the contribution of reactions involving the abstraction of hydrogen by methyl radicals from tetramethylsilane molecules and an increased yield of methane (G_{CH_4} = 4.8 mol./100 eV, while in the gas phase G_{CH_4} = 1.28 mol./100 eV). The yield of bis(trimethylsilyl)ethane and bis(trimethylsilyl)methane also increases with a corresponding decrease of the yield of ethane and ethyltrimethylsilane. The yield of "intrinsic" radical trapping agents—C_2H_4, C_2H_2, and C_3H_6—decreases by a factor of 50–100.

The thermal decomposition of organogermanium compounds, like that of organosilicon compounds, has been thoroughly investigated in connection with the necessity to prepare films of semiconducting germanium[15]. We may note that the thermal decomposition of organogermanium compounds is observed only above 350° C.

The available information about the radiation-thermal decomposition of organogermanium compounds is very scanty. Brinskman et al.[14] and Duval[24] disagree as regards the determination of the principal pathway in the decomposition of organogermanium molecules under the influence of radiation. Duval suggests that, even in the photochemical decomposition, the reaction involves the C–H bond and not the Ge–C bond, as claimed previously by Brinskman et al.[14] Magat and coworkers[25,26] demonstrated the formation of the $GeCl_3^{\cdot}$ radical and possibly also $GeCl^{\cdot}$ and the Cl_2^- ion ($G \simeq 0.5$) in the radiolysis of inorganic germanium halides.

In the determination of the radiation stability of tetraalkyl compounds of germanium it was shown[27] that an appreciable yield of the final radiolysis products is not observed in the field of ^{60}Co γ-radiation at 200° C over a period of 24 h: a germanium mirror is formed on the walls of the vessel at 250° C. Germanium tetrahalides do not undergo significant changes under analogous conditions.

The thermal decomposition of organotin compounds and their decomposition under the influence of electrons has been described in detail in a review[15]. The authors[15] note that the thermal decomposition of the majority of the organotin compounds investigated begins at ~ 300° C. Metallic tin is produced at an appreciable rate from an organotin compound at 200° C in the field of γ-radiation[27].

Dunn and Oldfield[28] investigated the radiolysis products of organotin compounds in benzene, hexane, and pentafluorobenzene. They showed that the radiolysis leads to the formation of traces of stepwise decomposition products:

$$R_3SnCl \rightsquigarrow R_4Sn + R_2SnCl_2 \quad ,$$
$$R_2SnCl_2 \rightsquigarrow R_4Sn + R_3SnCl + SnCl_4 \quad ,$$
$$RSnCl_3 \rightsquigarrow \text{residue} \quad ,$$
$$R_3SnOSnR_3 \rightsquigarrow R_2SnO.$$

The action of radiation on ethyltrimethylstannane and tetramethylstannane results in the formation of mainly the trialkylstannyl radical. The radiolysis of tetrabutylstannane in pentafluorobenzene leads to the formation of dibutyldifluorostannane (0.1%) and tributylfluorostannane (7.8%). The preferential formation of the trialkylstannyl radical during radiolysis is consistent with mass-spectrometric data for the elimination of alkyl groups from alkyl compounds of tin[29]. Irradiation of tetramethylstannane at 77 K also leads to the dissociation of the C–H bond and the formation of the $CH_3Sn{-}CH_2^{\cdot}$ radical. Prolonged irradiation results in the formation of species with an average number of tin atoms less than unity (in contrast to photolysis). Metallic tin is not produced during radiolysis[30-32].

As regards organolead compounds, it is known only that, in contrast to tetramethylstannane, irradiation of tetramethylplumbane at low temperature is accompanied by the liberation of metallic lead[33] and that its radiolysis in the gas phase leads to a complex mixture of products[34,35].

The available data on the radiolysis of organometallic compounds of Group IVB elements show that the dissociation of the element–carbon bond is one of the main pathways to the decomposition of the molecule under the influence of high-energy radiation. This suggests that the use of radiation methods in organometallic synthesis is desirable.

III. RADIATION-CHEMICAL HYDROMETALLATION

Reactions involving addition to a carbon–carbon double bond proceed in high yields via a radical-chain mechanism. Many examples of the initiation of such reactions by ultraviolet light are known[36]. The overall mechanism of reactions involving addition to a double bond can be represented by a series of consecutive or parallel stages[6].

(1) The generation of a free radical as a result of the action of ionising radiation on the molecule of the substance undergoing addition (the addend):

$$M \rightsquigarrow R^{\cdot} \quad , \tag{1}$$

where $R^{\cdot}$ is the chain propagating radical. The efficiency of the action of radiation depends to a large extent on the ability of the addend to decompose in the field of radiation with formation of free radicals.

(2) Initiation of the chain reaction as a result of the addition of the carrier radical to the double bond:

$$R^{\cdot} + R_1CH{=}CHR_2 \rightarrow R_1CHR{-}CHR_2^{\cdot} \quad . \tag{2}$$

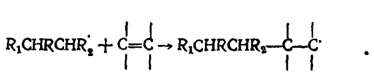
The rate of the second stage must be high, slow addition resulting in the formation of short chains and the possibility of dimerisation. The rate of reaction (2) is influenced by the structures of both the addend and the olefin. In the general case the rate of addition decreases on passing from ethylene to aromatic olefins in the sequence ethylene > substituted ethylenes > higher aliphatic alkenes > cycloalkenes > aromatic alkenes. Substitution by polar groups, for example halogens, lowers the reactivity of the double bond, but perhalogeno-compounds nevertheless react comparatively effectively. A terminal double bond is more reactive than an inner double bond. The $R^{\cdot}$ radical can in principle add to any carbon atom of a substituted ethylene, giving a mixture of isomeric products, but in each specific case the problem of the mode of addition requires special consideration[6].

(3) The complex radical $R_1CHR-CHR_2^{\cdot}$, formed in reaction (2), can in principle react in two ways: with the olefin or with an addend molecule. If the addend molecule is attacked by the carrier radical, we have the "normal" propagation of the chain reaction:

$$R_1CHR-CHR_2^{\cdot}+M\rightarrow R_1CHRCH_2R_2+R^{\cdot} \quad , \qquad (3)$$

etc.

(4) The radical formed in reaction (2) attacks an olefin molecule



$$R_1CHRCHR_2^{\cdot}+\overset{|}{\underset{|}{C}}=\overset{|}{\underset{|}{C}}\rightarrow R_1CHRCHR_2-\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}^{\cdot} \quad . \qquad (4)$$

The reaction results in the formation of polymeric products.

(5) The radical formed via reaction (4) may attack an addend molecule with formation of a chain-propagating radical (a carrier radical) and a 1 : 2 adduct (a telomerisation reaction). Adducts with compositions corresponding to a ratio greater than 1 : 3 are rarely encountered.

A mechanism agreeing with the general scheme[37,38] has been demonstrated in many instances for compounds of Group IVB elements.

Chain initiation:

$$HSiCl_3 \rightsquigarrow H^{\cdot}+SiCl_3^{\cdot} \quad , \qquad (1')$$

$$SiCl_3^{\cdot}+CF_2=CF_2\rightarrow CF_2-CF_2SiCl_3^{\cdot} \quad . \qquad (2')$$

Chain transfer:

$$CF_2CF_2SiCl_3^{\cdot}+HSiCl_3\rightarrow CHF_2CF_2SiCl_3+SiCl_3^{\cdot} \quad . \qquad (3')$$

Chain termination:

$$CF_2CF_2SiCl_3^{\cdot}+H^{\cdot}\rightarrow CHF_2-CF_2SiCl_3 \qquad (4')$$

Telomerisation:

$$CF_2CF_2SiCl_3^{\cdot}+CF_2=CF_2\rightarrow CF_2CF_2CF_2CF_2SiCl_3^{\cdot} \quad .$$

The reaction mechanism for alk-1-enes can be represented similarly[38]:

$$HSiCl_3 \rightsquigarrow H^{\cdot}+SiCl_3^{\cdot} \quad ; \qquad (1'')$$

$$SiCl_3^{\cdot}+RCH=CH_2\rightarrow RCHCH_2SiCl_3^{\cdot} \quad ; \qquad (2'')$$

$$RCHCH_2SiCl_3^{\cdot}+HSiCl_3\rightarrow RCH_2CH_2SiCl_3+SiCl_3^{\cdot} \quad . \qquad (3'')$$

Stage (3) is rate-determining for the reactions of simple olefins. Stage (4′) plays a major role when more complex unsaturated compounds, such as allyl chloride, allyl acetate, and *cis*-1,2-dichloroethylene, are involved in the reaction. It leads to the formation of 1 : 2 adducts and high-boiling compounds[38].

Radical-chain mechanisms of the type quoted above describe satisfactorily the majority of reactions of silicon compounds with olefins, but Lampe et al.[39] believe that an ionic mechanism operates in the addition reactions of unsubstituted silanes:

$$SiH_4 \rightsquigarrow SiH_3^{+}+H^{\cdot}+e \quad ,$$

$$CH_2=CH_2+SiH_3^{+}\rightarrow CH_2-CH_2SiH_3^{+} \quad ,$$

$$CH_2-CH_2SiH_3^{+}+SiH_4\rightarrow CH_3CH_2SiH_3+SiH_3^{+} \quad ,$$

etc.

The literature data for the interaction of silicon compounds with olefins in the field of ionising radiation are fairly extensive. Studies by various workers have made it clear that the structure of the silane undergoing addition has a decisive influence on the result of the reaction. It is essential to distinguish the following main cases: unsubstituted silanes of the type SiH_4; silanes substituted only by organic groups (alkylsilanes of the type R_nSiH_{4-n}); silanes substituted by halogens as well as organic groups (alkylchlorosilanes); silanes substituted by halogens only; finally, silanes without a hydrogen atom, for example, tetrachlorosilane. The reactivity of many aliphatic silicon compounds increases with respect to the double bond in the sequence

$$R_3SiH < R_2SiHCl < RSiHCl_2 < HSiCl_3 \quad .$$

This can be accounted for by a decrease in the above sequence of the hydride character of the hydrogen atom, which facilitates the homolysis of the Si–H bond under the influence of radiation.

An increase of the rate of reaction of aromatic compounds has been observed[40] on passing from dichlorophenylsilane to chlorodiphenylsilane and triphenylsilane. Apart from the unusual addition mechanism postulated by Lampe et al.,[39] the possibility of stepwise addition with formation of products having the structure $CH_3CH_2SiH_2CH_2CH_3$ together with 1 : 1 and 1 : 2 adducts should be noted for unsubstituted silanes[41]. Methylsilane and dimethylsilane mixed with ethylene (in proportions of 1 : 3 or 1 : 5) react in the gas phase[39,42] at 50°C to give a 1 : 1 adduct with the radiation-chemical yield $G = 38$ mol./100 eV and a 1 : 2 adduct with a yield of 15 mol./100 eV. Triphenylsilane adds to cyclohexene and oct-1-ene[43] under the conditions of γ-irradiation to give low yields of cyclohexyltriphenylsilane and octyltriphenylsilane. A comparatively high yield of nonyltriphenylsilane (radiation-chemical yield $G = 200$ mol./100 eV and a chemical yield of 66%) was obtained in the reaction with non-1-ene[44].

Under analogous conditions, naphthenes give very low yields, while alk-2-enes hardly react at all. The addition of alkylsilanes to vinylsilanes is of interest[45]:

$$(C_6H_5)_3SiH+(C_6H_5)_3SiCH=CH_2 \rightsquigarrow (C_6H_5)_3SiCH_2CH_2Si\,(C_6H_5)_3 \quad .$$

Very small yields have been obtained, but an increase of the latter may be expected when sources with a higher power are used.

Silanes containing chlorine atoms together with organic substituents react more vigorously. A radiation-chemical yield of ~ 200 mol./100 eV is reached in many reactions, the chemical yield amounting to ~ 50% under these conditions (80% for high doses). A large number of organosilicon compounds have been obtained by the radiation-chemical addition of alkylchlorosilanes to olefins with different structures (ethylene, propene, hexafluoropropene, cyclopentene)[30,40,46,47]. The main studies in this field have been carried out by Zimin and coworkers[47]. The authors found that the yields of products in reactions with unsaturated hydrocarbons vary appreciably with temperature, while those of reactions with fluoro-olefins are independent of temperature.

Among silicon compounds, trichlorosilanes are the most reactive in relation to olefins. The yield reaches 10^3 mol./100 eV in the radiation-initiated addition to olefins. The addition of trichlorosilane to ethylene, isobutene, C_5-C_8 alk-1-enes, certain alk-2-enes, cyclopentene, cyclohexene, allyl chloride, allyl acetate, 1,2-dichloroethylene, and polyfluoroalkenes has been described[38,40,46,47].

On the basis of the mechanism of the addition reaction described, one may assume that silicon compounds without hydrogen atoms are incapable of adding to olefins. On the other hand, it is known that the halides of certain elements, for example phosphorus[48,49], do add to olefins under the influence of ionising radiation. The data available at the present time do not allow an unambiguous answer to the question concerning the possibility of the addition to olefins of organosilicon halides without a hydrogen atom.

In the radiolysis of a mixture of tetrachlorosilane with methyl methacrylate and styrene[50], addition products were not isolated and only polymerisation of the above monomers was initiated. Shostenko et al.[51] attempted to add tetrachlorosilane and tetrachlorogermane to alk-1-enes. The addition products were isolated but the radiation-chemical yield proved to be very low (~ 1 mol./100 eV) and the process was complicated by many side reactions.

The nature of the addend plays a decisive role in radiation-chemical hydrosilylation reactions, but the nature of the olefin in many cases also alters the course of the reaction significantly. Thus γ-irradiation of a mixture of trichlorosilane and vinyl acetate leads to the formation of ethyl 2-trichlorosilyl ether apart from the 1 :1 and 1 :2 adducts. By selecting the reactant ratio, it is possible to make the reduction of the carbonyl group to the methylene group the main process[52]. The reaction of allyl derivatives is complicated by the formation of telomers[41,46] of the type $CH_3CH(X)CH(X)CH_2Y$, where $X=CH_2Cl$ or CH_2OOCH_3 and $Y=SiCl_3$ or $SiCl_2CH_3$. It was noted in a study of the hydrosilylation of polychlorofluorocyclobutene, polyfluorocyclobutene, and cyclopentene initiated by γ-radiation that the presence of an organic substituent at the silicon atom greatly retards the reaction[53,54]. Apart from the expected addition products, reduction products were obtained as a result of the exchange of Cl atoms for hydrogen atoms. The reactivity decreases on passing from butenes to pentenes[53,54].

The addition of germanium compounds to olefins in the field of ionising radiation has been scarcely investigated; this problem is merely touched on in the study mentioned above[51].

Liquid-phase hydrostannylation takes place with a high radiation-chemical yield at room temperature[55,56]. Kocheshkov and coworkers[57] developed a method for the radiation-chemical hydrostannylation in order to synthesise many organotin compounds, including those which are difficult to obtain or which have been described for the first time. The authors showed that, in contrast to hydrosilylation, radiation-chemical hydrostannylation takes place at room temperature. Low reaction temperatures are responsible for the specific reaction pathway leading to the formation of products of the "normal" addition to the double bond. Side products or products of the polymerisation of the initial olefins have scarcely been detected. The reaction has been carried out for olefins having different structures: hex-1-ene, hept-1-ene, oct-1-ene, styrene, allyl alcohol, etc; the radiation yield is ~ 10^3 mol./100 eV in all cases.

A study of radiation-chemical hydrostannylation[58] using triethylstannane and hept-1-ene as a model showed that the rate of reaction is described by S-shaped kinetic curves, which are typical of branched-chain processes. The activation energy (1.5 kcal $mole^{-1}$) shows that the role of temperature as a factor increasing the rate of the process is in this case small. The relation between the rate of reaction and the dose rate is quadratic; the induction period observed at low dose rates (2 h for 5 rad s^{-1}) diminishes with increasing dose rate; when irradiation is interrupted, the reaction stops.

IV. DIRECT SYNTHESIS IN THE FIELD OF IONISING RADIATION

The interaction of metals with alkyl halides (direct synthesis) is an important method for the preparation of organometallic compounds:

$$M + RHal \rightarrow RMHal\ ,$$

where M is the metal, R the organic group, and Hal the halogen. Group IVB elements react with alkyl halides under severe temperature conditions, which differ strongly depending on the nature of the metal and the halogen atom and the reaction temperature is frequently above the limit corresponding to the pyrolytic decomposition of alkyl halides. For example Rochow's method, used nowadays for germanium, consists in passing the alkyl halide vapour over a germanium-copper mixture heated to 300–350° C; alkyl halides containing more than four carbon atoms decompose under these conditions. It is necessary to carry out special studies in order to intensify the direct synthesis and to find milder reaction conditions.

The usefulness of radiation in direct synthetic reactions is based on the following considerations. It follows from studies of the mechanism of the direct synthesis in recent years that electron transfer from the metal atom to the molecule of the organic halide is the most important stage of the reaction of the metal with the alkyl halide, responsible for the formation of the M–C bond[59-63]. Electron transfer results in the formation of active radical species. (The ideas about the mechanism of the direct synthesis of organosilicon and organogermanium compounds are developing mainly in relation to catalytic gas-phase processes involving copper[64,65].) It is appropriate to mention here that the formation of organic radicals (for example by irradiation) promotes a more vigorous direct synthesis. The formation of radicals in the radiolysis of alkyl halides has been frequently observed even in early investigations[66,67]; subsequently it was shown that, with increase of temperature, radiation-induced processes in liquid alkyl halides (isomerisation) may take place quantitatively[68].

The influence of γ-irradiation on the direct synthesis was investigated for the first time by Kocheshkov and coworkers[69,70] in the reaction between powdered tin and butyl bromide. They showed that, in the absence of irradiation, tin does not react with boiling butyl bromide, while on irradiation with ^{60}Co γ-rays the reaction proceeds at an appreciable rate even at room temperature. The radiation-chemical yield is 50–58 mol./100 eV. The lack of thermal experiments under comparable conditions precludes the consideration of the magnitude of the effect of irradiation, but in this instance any decrease of reaction temperature below the boiling point of the alkyl halide is of great practical importance: the necessity for employing an excess pressure during the reaction is obviated.

Subsequently research on the radiation-chemical synthesis of organotin compounds was developed in order to devise an experimental industrial plant[71-82]. The study of the process over a wide temperature range showed that the radiation-chemical yield may be increased to 10^3 mol./100 eV.

The interaction of metallic tin and alkyl halides is an extremely complex process, the rate and direction of which depend significantly on many factors: the nature of the initial reactants and their mass ratio, temperature, dose rate, rate of stirring of the reaction mixture, and the presence of impurities. It has been shown that the reaction is to a large extent specific, with formation of dibromodibutylstannane and a certain amount of bromotributylstannane[69,70]. An increase of temperature accelerates the reaction[71], the optimum temperature of the synthesis of dibromodibutylstannane being 95° C; a further increase of temperature leads to a decrease of the reactivity of tin, probably owing to its aggregation. Temperature also influences the proportions of the final products: when the temperature is reduced, the content of tribromobutylstannane increases. According to Vereshchinskii and coworkers[72], the effective activation energy is 12 kcal mole^{-1}, while according to Fentiman and coworkers[81,82] it is 35 kcal mole^{-1} at 95° C and shows a tendency to vary with temperature. By varying the irradiation dose rate from 0.7 to 220 rad s^{-1}, it has been shown that the rate of reaction is proportional, other conditions being equal, to the square root of the absorbed dose rate. In the synthesis of dibromodibutylstannane under optimum conditions the radiation-chemical yield is 1600–2100 mol./100 eV. The radiation-chemical yield varies with the length of the carbon chain in the alkyl halide, decreasing with increase in chain length.

Vereshchinskii and coworkers[78] and Fentiman and coworkers[81,82] noted an appreciable induction period in the reaction and discussed various methods for eliminating it[79,81]. The preparation of the tin surface, the particle size, and the method of obtaining tin affect both the rate of the process and the proportions of the reaction products[71,72,81].

It is noteworthy that the nature of the halogen in the alkyl halide is very important. Alkyl chlorides do not react[82]. The effect of irradiation in the reaction of alkyl halides with a mobile halogen atom, for example, allyl bromide, is manifested by a decrease of the induction period[83].

The effectiveness of the influence of γ-radiation on the direct synthesis of organotin compounds stimulated research on the role of γ-radiation in the direct synthesis of organogermanium compounds. The influence of radiation and the reaction between germanium and alkyl bromides has been studied by Kocheshkov and coworkers[84,85]. It has been shown that γ-radiation has different effects on the direct synthesis of organogermanium compounds in the liquid and gas phases. Under steady-state conditions, gaseous butyl bromide reacts with germanium powder at 240° C over a period of 13 h only to an extent of 10–12%, while on γ-irradiation (at a dose rate of 100 rad s^{-1}) the extent of the reaction is 20–25% even at 160° C, i.e. the temperature of the onset of the reaction under irradiation conditions is reduced by 100° C. At 220–230° C the germanium charge has been consumed to an extent of 80–85%, i.e. almost quantitatively. The radiation-chemical consumption of germanium (at 200° C) after 13 h amounts to 5×10^2 mol./100 eV, which indicates a chain mechanism of the process. In the liquid phase the influence of γ-radiation is much weaker: the temperature thresholds of the reactions of germanium with butyl bromide and hexyl bromide are reduced by only 20° C. The temperature dependence of the degree of reaction also shows that the thermal stage plays an important role in the liquid phase. The radiation-chemical consumption of germanium in the liquid phase is $\sim$ 50 mol./100 eV.

The quantitative compositions of the products obtained under the influence of γ-radiation in the gas and liquid phases are different. In the liquid-phase reaction the main product is tribromobutylgermane, as in the experiments without irradiation. A mixture of tribromobutylgermane and germanium tetrabromide in proportions of 1 : 3 is obtained in the gas phase. The radiation-chemical yields of tribromobutylgermane in the liquid and gas phases are approximately the same, amounting to 50 mol./100 eV under the following conditions: 200° C, reaction time 13 h. Thus γ-radiation makes it possible to reduce appreciably the temperature of the reaction of germanium with gaseous alkyl halides, but it leads to the formation of an undesirable product—germanium tetrabromide. The process occurring in the gas phase under the influence of γ-radiation can be driven towards the formation of organogermanium compounds by adding copper. In the presence of copper, the content of germanium tetrabromide in the reaction mixture decreases and the yield of tribromobutylgermane increases[84,85].

V. THE EFFECT OF RADIATION ON THE RADICAL REDISTRIBUTION REACTION

If it is assumed that the rate of the radical redistribution reaction

$$R_4M + MX_4 \rightleftarrows \Sigma R_nM_{4-n}$$

depends on the M–C bond strength, one may postulate a stimulating effect of γ-radiation since the molecules of the initial organometallic compounds decompose in the field of ionising radiation at the M–C bond[23-26,29].

Kocheshkov et al.[86] found that the reaction between tetra-alkylstannane and germanium tetrahalide in the field of γ-radiation can be carried out at room temperature. In the absence of radiation the analogous reaction takes place above 200° C.[87,88]

The reaction between tetra-alkylstannane and germanium tetrahalide takes place with transfer of only one organic group regardless of the initial reactant ratio, in contrast to the analogous reaction between tetra-alkylstannane and tin halides. Under the joint influence of radiation and an increased temperature, the abstraction of a second organic group from tetra-alkylstannane is observed, but only monosubstituted organogermanium compounds are formed[27]. The reaction proceeds in accordance with the equation

$$R_4Sn + 2GeHal_4 \rightarrow R_2SnHal_2 + 2RGeHal_3 \ .$$

The thermal radical redistribution reaction between tetra-alkylstannane and germanium tetrahalides takes place only in the presence of a catalyst. Under the influence of radiation, the reaction may be carried out at 200° C with transfer of a single organic group[89].

VI. REACTIONS UNDER THE INFLUENCE OF IONISING RADIATION NOT INVOLVING THE METAL–CARBON BOND

Chlorination, oxidation, and polymerisation reactions, which are fairly well known in the radiation-chemical synthesis of organic compounds, can be in principle initiated by irradiation of the organic group[2-4]. However, there are few experimental data concerning Group IVB elements. Dzhagatspanyan and coworkers[90-93] investigated the radiation-chemical chlorination of organochlorosilanes. The radiolysis of a mixture of chlorine and dichlorodimethylsilane leads to the formation of a 30% yield of a monochloro-substituted product with traces of a dichloro-product. The composition of the chlorination products is independent of temperature and the yield is only slightly temperature dependent. The yield is also independent of the dose rate, but decreases significantly in the presence of oxygen. In the reactions of dichloromethylphenylsilane and trichlorophenylsilane the result depends significantly on temperature. Vigorous incorporation of chlorine in the benzene ring, analogous to that in photochemical chlorination, is observed in the range 0–20° C, but above 100° C ring substitution begins; both processes take place simultaneously at intermediate temperatures. Oxygen does not inhibit the reaction at 100–150° C, which suggests an ionic reaction mechanism. Substitution in the methyl group was not observed under the conditions of radiation-chemical chlorination.

Table 1. Radiation-induced reactions of silicon, germanium, tin, and lead compounds.

Compound	Irradiation conditions	Radiolysis products	Radiation-chemical yield, mol./100 eV	References
R_4Si	electron-beam decomposition gas phase, 150°C	Si	—	15, 16
	X-rays, gas phase, 4.2×10^{17} eV ml^{-1}	H_2, C_2H_6, CH_4, $C_2H_5Si(CH_3)_3$, $(CH_3)_6Si_2$	>10	18, 19
	γ-rays, solid phase, -130--180°C	—	~5	20—22
	liquid phase, 25°C	CH_4, $(CH_3)_3Si-CH_2CH_2-Si(CH_3)_3$, $(CH_3)_3Si-CH_2-Si(CH_3)_3$	>10	23
R_4Ge	γ-rays, 24 h, 100 rad s^{-1}	Ge	—	27
$RGeCl_3$	solid phase, -196°C	$HGeCl_3$, $GeCl_4$	—	14
$GeCl_4$	solid phase	—	0.5	25, 26
R_4Sn	γ(^{60}Co), solid phase, 200°C, 100 rad s^{-1}	Sn	—	27
	X-rays, liquid and solid phases	$R_3Sn^{\cdot}$, $R_3SnCH_2^{\cdot}$	—	28—31
R_3SnCl	γ(^{60}Co), solvent, 25°C	R_4Sn, R_2SnCl_2, $SnCl_4$, R_2SnO	—	28
R_4Pb	γ(^{60}Co), solid, liquid, and gas phases	Pb	—	33—35

Table 2. The influence of irradiation on the reactions of free radicals with alkyl halides (direct synthesis).

Reactants	Reaction conditions	Radiation-chemical yield, mol./100eV	Chemical yield, %	Reaction products	References
Sn + RBr	γ(^{60}Co), liquid phase, 25-100°C	~10^3	80 (w.r.t. Sn charge)	R_2SnBr_2, R_3SnBr, $SnBr_2$	70—82
$Sn+CH_2=CH-CH_2Br$	γ(^{60}Co), 25°C	—	—	$(CH_2=CH-CH_2)_2SnBr_2$, $[(CH_2=CH-CH_2)_2SnBr_2]_n$	83
Ge + RBr	γ(^{60}Co), liquid phase, 100 rad s^{-1}, 250°C	~10^1	50 (w.r.t. Ge charge)	$RGeBr_3$	84—85
Ge + RBr	γ(^{60}Co), gas phase, 150-200°C	~10^2	50 (w.r.t. Ge charge)	$RGeBr_3$, $GeBr_4$	85

Table 3. The influence of irradiation on reactions leading to the replacement of an organic substituent or a functional group at the metal atom.

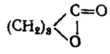
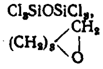
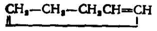
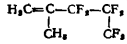
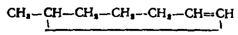
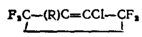
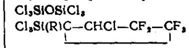
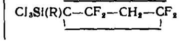
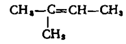
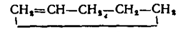
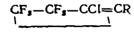
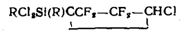
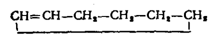
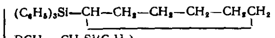
Reactants	Reaction products	Irradiation conditions	Radiation chemical yield, mol./100 eV	Chemical yield, %	Refs.
$R_4Sn + GeCl_4$	R_3SnCl, $RGeCl_3$	γ(^{60}Co), 20 Mrad, 25°C	—	50—90	86
$R_4Ge + GeBr_4$	R_3GeBr $RGeBr_3$	γ(^{60}Co), 10 h, 100 rad s^{-1}, 250°C	200	70—80	27, 89
$R'Cl+R_kHSiCl_{4-(k+1)}$	$R'R_kSiCl_{4-(k+1)}$	50-150°C	100÷600	60÷80	99, 103
 $+HSiCl_3$	$Cl_3SiOSiCl_3$, 	γ(^{60}Co), 0.185 Mrad h^{-1} 25°C	—	33÷81	104

Table 4. The influence of irradiation on the hydrometallation reaction.

A	Reaction products	Chemical yield, %	Radiation-chemical yield, eV mol./100 eV
$(C_2H_5)_3SnH$ + A [25°C, γ (^{60}Co), 2 × 10^6 rad] (Refs.56-58)			
$CH_2=CHC_5H_{11}$	$(C_2H_5)_3SnC_7H_{15}$	74.5	1000
$CH_2=CHC_6H_{13}$	$(C_2H_5)_3SnC_8H_{17}$	77	1000
$CH_2=CHC_8H_{17}$	$(C_2H_5)_3SnC_{10}H_{21}$	96	1000
$C_6H_5CH=CH_2$	$(C_2H_5)_3SnCH_2CH_2C_6H_5$	50	700
$C_6H_5C\equiv CC_6H_5$	$(C_2H_5)_3SnC_6H_5C=CHC_6H_5$	70	800
$C_6H_5C\equiv CH$	$(C_2H_5)_3SnCH=CHC_6H_5$	87.5	1200
$CH_2=CHCH_2OH$	$(C_2H_5)_3SnCH_2CH_2CH_2OH$	92.7	1500
$CH_2=CHOC_2H_5$	$(C_2H_5)_3SnCH_2CH_2OC_2H_5$	80	1300
$CH_2=CHOC_4H_9$	$(C_2H_5)_3SnCH_2CH_2OC_4H_9$	88	1300
$CH_2=CHCOOCH_3$	$(C_2H_5)_3SnCH_2CH_2COOCH_3$	74	1200
$(C_4H_9)_3SnH$ + A (25° C, 2 × 10^6 rad) (Ref.56-58)			
$CH_2=CHC_5H_{11}$	$(C_4H_9)_3SnC_7H_{15}$	85.9	960
$CH_2=CHC_6H_{13}$	$(C_4H_9)_3SnC_8H_{17}$	70	750
$C_6H_5CH=CH_2$	$(C_4H_9)_3SnCH_2CH_2C_6H_5$	97	2100
$C_6H_5C\equiv CC_6H_5$	$(C_4H_9)_3SnC_6H_5C=CHC_6H_5$	80	720
$CH_2=CHCH_2OH$	$(C_4H_9)_3SnCH_2CH_2CH_2OH$	81	2000
$CH_2=CHOC_2H_5$	$(C_4H_9)_3SnCH_2CH_2OC_2H_5$	92	1300
$CH_2=CHOC_4H_9$	$(C_4H_9)_3SnCH_2CH_2OC_4H_9$	99	1100
$CH_2=C(CH_3)COOCH_3$	$(C_4H_9)_3SnCH_2CH(CH_3)COOCH_3$	90.7	1000
$CH_2=CHCONH_2$	$(C_4H_9)_3SnCH_2CH_2CONH_2$	75	950
$(C_6H_5)_3SnH$ + A (25° C, 2 × 10^6 rad) (Refs.56-58)			
$CH_2=CHC_6H_{13}$	$(C_6H_5)_3SnCH_2CH_2C_6H_{13}$	73.6	700
$CH_2=CHCH_2OH$	$(C_6H_5)_3SnCH_2CH_2CH_2OH$	80	1200
$HSiCl_3$ + A [25°C, γ (^{60}Co), 3-9 Mrad] (Refs.38,46,47,52)			
$ClCH=CHCl$	$CH_2ClCHClSiCl_3$	27	—
$CF_2=CF_2$	$CHF_2CF_2SiCl_3$	11	—
	$C_5H_9SiCl_3$	96	—
$CF_3CF=CF_2$	$(C_3HF_6)SiCl_3$	95	—
$CH_2=CH-CF_2CF_3$	$C_2F_5(CH_2)_2SiCl_3$	—	—
$CH_2=CH-CF_2-CF_2-CF_3$	$C_3F_7(CH_2)_2SiCl_3$	52	—
 $H_2C=\underset{CH_3}{C}-CF_2-\underset{CF_3}{CF_2}$	$C_3F_7CH(CH_3)CH_2SiCl_3$	11	—
$CH_2=CH-CH_2Cl$	$ClCH_2(CH_2)_2SiCl_3$ $H(CH_2ClCHCH_2)_2SiCl_3$	40 34	— —
$CH_2=CH-CH_2-COO-CH_3$	$CH_3COO(CH_2)_3SiCl_3$ $H(CH_3COOCH_2CHCH_2)_2SiCl_3$	22 71	— —
	$C_6H_{10}(CH_3)SiCl_3$	92	—
$CH_2=CH-OCOCH_3$	$Cl_3SiCH_2CH_2OCH_2CH_3$ $Cl_3SiCH_2CH_2OCOCH_3$ $Cl_3SiOSiCl_3$	— — —	— — —
		12.8	—
		—	—
RCl_2SiH + A [25°C, γ (^{60}Co)](Refs. 38,46,47,53,54)			
$CH_3-CH=CH-CH_3$	$C_2H_5CH(CH_3)SiRCl_2$	57	—
 $CH_3-\underset{CH_3}{C}=CH-CH_3$		30	—
$CF_3-CF=CF_2$	$(C_3HF_6)SiRCl_2$	85	—
$CH_2=CH-CF_2-CF_2-CF_3$	$C_3F_7(CH_2)_2SiRCl_2$	23	—
$CH_2=CH-CH_2Cl$	$ClCH_2(CH_2)_2SiRCl_2$	4	—
	$C_5H_9SiRCl_2$	20	—
		12.8	—
R_nSiH_{4-n}+A[50°C, γ (^{60}Co), gas phase] (Refs.39,41,42)			
$CH_2=CH_2$	$(R_nSiH_{3-n})CH_2-CH_3$	—	—
$(C_6H_5)_3SiH$ + A[γ(^{60}Co)](Refs.43-45)			
		66	200
$RCH=CH_2$	$RCH_2-CH_2Si(C_6H_5)_3$	—	—
$CH_2=CH-Si(C_6H_5)_3$	$(C_6H_5)_3SiCH_2-CH_2-Si(C_6H_5)_3$	20	—

Irradiation of triethylvinyl-, trimethoxyvinyl-, triethoxyvinyl-, diethylvinyl-, dichloromethylvinyl-, and trichlorovinyl-silanes with ^{60}Co γ-rays leads to the formation of a viscous polymer with a radiation-chemical yield ranging from 20 to 320 mol./100 eV.[94,95] Both γ-initiated polymerisation and polymerisation under the influence of

β-rays have been investigated for allyl derivatives of silicon[96]. Triethylvinylstannane and triphenylvinylstannane polymerise[97] in the field of γ-radiation at 80°C with a radiation-chemical yield of 140–220 mol./100 eV. The polymerisation product consists mainly of dimers and trimers.

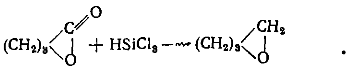
Certain reactions leading to a change in the mobile groups at the metal atom in the field of radiation have been described. The homolytic reduction of organic halides by silicon hydrides in the field of ^{60}Co radiation or in a stream of accelerated electrons, observed in early investigations[98], takes place under comparatively mild conditions:

$$RCl + HSiR'_3 \rightsquigarrow R'_3RSi + HCl \quad .$$

The reaction has been studied in a series of investigations by Zimin and coworkers[99–103]. The authors showed that, under the most severe conditions of synthesis, the temperature does not exceed 300° C, i.e. is less than the temperature of the radiation-chemical decomposition of organochlorosilanes. Fluorinated organic halides react at a lower temperature (100–120° C) than the non-fluorinated compounds (170–180° C), which has been shown for chlorobenzene and pentafluorobenzene. The activation energies for the reactions are respectively 2–4 and 12–13 kcal mole^{-1}. The average radiation-chemical yield is 600 mol./100 eV and a quadratic relation has been observed between the radiation-chemical yield and the dose rate.

The authors[99–103] concluded that the radiation-chemical reduction of organic halides by silicon hydrides is of interest as a convenient method for synthesising organosilicon compounds. The data obtained are sufficient to design an enlarged radiation-chemical plant for the synthesis of organochlorosilanes[102].

Inorganic silanes may be used for the radiation-chemical reduction of organic compounds: the quantitative synthesis of cyclic ethers from lactones has been described[104]:



In conclusion we may note that ionising radiation has a significant influence in many instances (Tables 1–4)† on the chemical reactions of the elements under consideration. This factor can be used successfully in practical synthesis.

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†In the tables R stands for aliphatic radical and γ(^{60}Co) for γ radiation from a ^{60}Co source. As in the original reports, the tables list the maximum yields.

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The Photochemical and Radiation-chemical Stability of Molecules. Unimolecular Reactions Involving the Abstraction of a Hydrogen Atom

V.G.Plotnikov and A.A.Ovchinnikov

The ways in which electronically excited molecular systems are deactivated are examined, a theory of the non-adiabatic and predissociation mechanisms for the decomposition of molecular systems with elimination of a hydrogen atom is described, and the isotope effect in this reaction is discussed and compared with experimental data. The photochemical stability of molecules of different classes, radical-cations, and radicals is explained on the basis of the theoretical results. The evolution of atomic hydrogen (formation of radicals) in low-temperature radiation-chemical experiments is associated with the position of the lowest triplets state of the molecules, their ionisation potentials, the polarity of the medium, and the energies of the C-H bonds in the radical-cations.

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I. INTRODUCTION

One of the fundamental problems in photochemistry and radiation chemistry is that of the relation between the structure of molecules and their resistance to the action of radiation. The theoretical aspects of this problem are examined below for unimolecular reactions involving the abstraction of a hydrogen atom. Reactions of this type are some of the most common in the photochemistry and radiation chemistry of hydrogen-containing compounds[1-3].

Correct ideas about the relation between the structure of molecules and their stability were put forward for the first time by Voevodskii and Molin[4], who related the stability of the molecule to the energy of its lowest excited state. According to their hypothesis[4], molecules in which the energy of the first excited singlet state exceeds the bond dissociation energy are unstable; when the opposite situation obtains the molecular stability increases sharply. It has been shown[5,6] that the decomposition of electronically excited complex molecules with elimination of a hydrogen atom can proceed with an appreciable probability via a predissociative mechanism only in triplet states and molecular stability must therefore be related to the positions of the lowest triplet state. The approaches on which the studies of Voevodskii and Molin[4] and Plotnikov[5,6] were based are similar, the difference consisting only in the nature of the states involved in the molecular decomposition. However, this does not mean by any means that the conclusions reached by the two sets of workers lead to identical results, since there exist molecules (for example the benzene molecule) in which the energy of the lowest triplet state is lower than that of the bond undergoing the dissociation, while that of the lowest singlet state is higher.

The explanation of the radiation-chemical stability of molecules towards the elimination of hydrogen atoms solely with allowance for the decomposition of electronically-excited molecules[2,4,7,8] cannot be complete, because hydrogen atoms can also be formed in the decomposition of electronically-excited radical-cations. The mechanism of the non-adiabatic decomposition of molecular radical-cations, radicals, and molecules with elimination of a hydrogen atom has been discussed[9] and it has been shown that the probability of the reaction is determined mainly by the energy of the bond undergoing dissociation, which is large for molecules and cannot be small for radicals and radical-cations.

In all the studies quoted above, it was assumed that the decomposition with elimination of a hydrogen atom proceeds in electronically excited states. In principle, there is a possibility of another decomposition mechanism, reducing to the transformation of electronic energy into the vibrational energy of the system with its subsequent concentration, by fluctuations, in the bond undergoing dissociation. The rate of such a process ($\sim 10^6$ s^{-1} for molecules with only a few atoms) decreases exponentially with increase of the number of vibrational degrees of freedom of the system[10,11]. Hence it will be necessary to conclude that the stability of the molecules increases with increase of their complexity and that polymeric molecules are stable, which conflicts with experimental data[1-3]. The independence of pressure of the quantum yield of hydrogen atoms[12,13] also shows that the contribution of the fluctuation decomposition mechanism is small, because otherwise an increase of pressure, which leads to an increased rate of vibrational relaxation, should decrease the yield. In a condensed phase the quasi-equilibrium mechanism of the decomposition of polyatomic systems[10,11] is still less likely, since the lifetime of the vibrationally excited states is extremely short (10^{-11} to 10^{-12} s) in consequence of the vigorous vibrational relaxation processes, which suppress the decomposition process. In the case of systems with only a few atoms (CH_4, H_2O) the vibrational relaxation time is long—up to 10^{-2} s, and the fluctuation mechanism of their decomposition in the ground electronic state (!) cannot be fully ruled out[14-16].

The attempts to describe photochemical reactions with elimination of a hydrogen atom by a mechanism involving a redistribution of vibrational energy cannot be regarded as satisfactory, because they either did not account for the vibrational relaxation[17], or dealt with $\sigma\sigma^*$ and $n\sigma^*$ states of molecules with only a few atoms[18], for which the potential surface is not of the bonding type, and consideration of the redistribution of vibrational energy to a large extent lacked physical significance. It follows from the foregoing that the decomposition of polyatomic electronically excited systems takes place without passing through the stage of the redistribution of vibrational energy by fluctuations. Direct experimental and theoretical evidence for this conclusion will be presented later.

The ways in which electronically excited molecular systems are transformed and the mechanism of the elimination of a hydrogen atom will be considered below, and on this basis the photochemical and radiation-chemical stability of molecular systems will be explained. Since the experimental data for this process have been described systematically in a number of monographs[1-3,19-21] and reviews[22,23], we confined ourselves to giving references to these sources, using the data of original studies only when necessary.

II. ELECTRONIC ENERGY LEVELS OF MOLECULAR SYSTEMS

This section presents information about the nature of the electronically excited states of molecular systems required for further consideration. The Hamiltonian of a molecular system H can be formulated as the sum of the Hamiltonian in the adiabatic approximation H_0, the non-adiabatic operator V, and the spin–orbital interaction operator H_{so}. The eigenfunctions of the Hamiltonian H_0 consist of product of electronic, vibrational, and rotational functions. For a condensed phase, the rotational motion of polyatomic systems is impossible, and one need consider only the electronic and vibrational functions and the corresponding states.

The states of a system with a Hamiltonian H_0 are characterised by a definite electron spin and may be classified in terms of the multiplicity. The majority of molecules have a singlet ground state (S_0) and can have both singlet (S_1, S_2, ...) and triplet (T_0, T_1, ...) electronically excited states. The triplet state T_0 is the excited state of molecules with the minimum energy. The first excited S_1 state lies somewhat above (by 10^3–10^4 cm^{-1}) the triplet state T_0. Other triplet states are frequently distributed between the T_0 and S_1 states[24]. The ground and first electronically excited states of singly charged radical-ions and radicals derived from organic molecules are doublets. There is very little information about the distribution of quartet states in these systems and they are apparently usually located above the first excited state. (As an example, one may quote the allyl radical, for which calculations with complete allowance for the configuration interaction in terms of the π-electron approximation[25] have shown that the quartet level lies above the first excited doublet.)

Another important characteristic of the electronic states of molecular systems is their orbital nature, determined by the nature of the electronic transition which results in the given state. In molecules of organic compounds it is possible to distinguish three types of electrons: π, σ, and n. The wave function of π and σ electrons are delocalised over the molecule. (In molecules containing heteroatoms, there naturally exist π and σ orbitals, with the maximum values corresponding to the location of the heteroatom. This maximum is usually low and the wave function is delocalised over the entire molecule.) The n-electron wave function is non-zero only in a limited region of the molecular system. The π- and σ-electron orbitals can be both bonding and antibonding, and are designated in the latter case by π^*, and σ^*; n-orbitals are non-bonding.

In conformity with the foregoing, electronic states of the following types are possible in molecular systems: $\pi\pi^*$, $\sigma\sigma^*$, $n\sigma^*$, $\sigma\pi^*$, $\pi\sigma^*$, and $n\pi^*$; these arise as a result of electronic transitions between the above orbitals. All these states are characterised by a definite multiplicity. In molecular spectroscopy and photochemistry the following notation has been adopted for electronic states, indicating their multiplicity and electronic nature: $S_{\pi\pi^*}$, $T_{\pi\pi^*}$, $S_{n\pi^*}$, $T_{n\pi^*}$, etc. (We may note that the eigenvalues of the Hamiltonian H_0 corresponds to these states and are not mixed under the influence of the operators V and H_{so}. This classification is possible if the distance between the states is significantly greater than the matrix elements of the operators V and H_{so}, which never exceed ~100 cm^{-1}.) For further consideration, it is important to note that, in all the states except $n\pi^*$ and $n\sigma^*$, the electrons are delocalised over the molecular system. Electrons in the $n\pi^*$, and $n\sigma^*$ states are localised near the heteroatom containing the n electrons.

The radical-cations derived from long paraffinic molecules occupy a special place among molecular systems[26]. Despite the fact that the ground state is of the σ-type, it is localised in a fairly small region of the large molecule. The reason for this is that, on localisation of a hole in the middle part of the molecule, the energy decreases by approximately 0.5 eV owing to the change in the C–C bond length. The localisation region then corresponds to 4–5 bond lengths (6–7 Å).

The electronic excitation of the molecular system entails a change in bond lengths (and in the general case also in bond angles) and in vibration frequencies. The rate of non-adiabatic transitions, including transitions involving the fragmentation of the molecular system, depends on these parameters and also on the extent to which the corresponding vibrations are anharmonic. The changes in bond lengths and vibration frequencies on electronic excitation may be inferred from the vibronic absorption and luminescence spectra of molecular systems. Together with vibrational spectra, they make it possible to determine also the anharmonicity of the vibrations. For many compounds, particularly aromatic compounds and their derivatives, these spectra have been investigated[24,27-29] and it has been found that (1) the change in the vibration frequencies of polyatomic molecules on electronic excitation is small in most cases compared with the vibration frequencies†; (2) the changes in bond lengths are also

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† An appreciable change in the vibration frequencies of the C–O group is observed on $n \rightarrow \pi^*$ transitions in carbonyl compounds[27], which is due to the local nature of the transition.

small and, what is particularly important for further discussion, there is no significant change in the C–H bond lengths regardless of the nature of the state; (3) the majority of molecular vibrations can be described in terms of the harmonic approximation but the stretching vibrations of the C–H bonds (and in general R–H bonds) exhibit appreciable anharmonicity. The last conclusion is valid for any system containing a hydrogen atom, because the anharmonicity of the vibrations increases with decrease in the reduced mass of the oscillator.

The absorption spectra of aliphatic compounds are as a rule structureless[1] and it is therefore difficult to determine from them the change in the geometrical parameters of the molecule on electronic excitation. However, one may make the general claim[5,30] that the changes in these parameters are small, in molecules containing a large number of identical bonds, after $\pi \rightarrow \pi^*$, $\sigma \rightarrow \sigma^*$, $\sigma \rightarrow \pi^*$, and $\pi \rightarrow \sigma^*$ electronic transitions if one considers states with a comparatively low energy, not exceeding 10 eV (see Section VII). Since the electronic transitions in the above energy range are due to the delocalised electrons of the C–C bonds and the bonds between carbon atoms and the heteroatom[31,32], electronic excitation should alter the lengths of these bonds alone; the C–H (and in general R–H) bonds change insignificantly. This applies also to $n\pi^*$ and $n\sigma^*$ states. Few data are available at present for the electronic spectra of radical-cations (see Pshezhetskii et al.[19] and Bogatyreva and Buchachenko[22] together with the literature which they quote). However, for reasons stated above, one may assume that in these systems too the changes in bond lengths on electronic excitation are small and, what is most important, frequently do not involve the C–H (R–H) bonds.

The above conclusions, which follow from experimental data and theoretical considerations, constitute the basis of the theoretical models for reactions involving the elimination of a hydrogen atom. Certain deviations from such models will be indicated below (see Section VIII).

III. DEACTIVATION PROCESSES INVOLVING EXCITED MOLECULAR STATES

Following optical excitation or excitation by electron impact, the molecular system passes from the ground electronic states to an excited state (in the general case a vibronic state), which corresponds to an eigenvalue of the Hamiltonian H_0. For a long time, this postulate was assumed without proof and conditions under which it is valid were established only comparatively recently[33,34]. These conditions reduce to the following: (1) in the region of the excitation energy there is one state of the system with the Hamiltonian H_0 to which transition from the ground state is allowed; (2) the excitation is due to a source whose spectral line width exceeds the width of the excited state[35]. In classical (non-laser) photochemistry and radiation-chemistry the above conditions are fulfilled.

This applies not only to a free molecule, but also to a molecule in a solvent. In this case, during the first instant after excitation, the system is also in a state which is an eigenstate of the Hamiltonian H_0. (For this, it is necessary that the interaction of the vibrations of solvent molecules with the electronic excitation in the given molecule should be weak.) If the initial state is vibrationally excited, it relaxes owing to the interaction of the vibrations of the molecule of the compound with those of the molecules of the solvent. In polyatomic systems the rate of vibrational relaxation is extremely high, amounting to $10^{11}-10^{13}$ s^{-1}.[24] In molecular systems consisting of a small number of atoms (H_2, N_2, CH_4, etc.) the rate of vibrational relaxation may be much smaller (down to 10^{-2} s^{-1}), as stated above, and may depend very markedly on the amount of vibrational energy[14]. This effect is due to the relatively small number of vibrational modes in such systems and the anharmonicity of the vibrations.

The states of the Hamiltonian H_0 are not eigenstates of the system Hamiltonian H and therefore undergo spontaneous radiationless decomposition under the influence of the operators V and H_{SO}. Irreversible radiationless decomposition can occur only when the system in the final state has a continuous (quasi-continuous) energy spectrum[33,34,36,37]. Polyatomic molecules have a quasi-continuous spectrum of vibrational levels when the vibrational excitation energies exceed 1 eV. In the case of molecules with only a few atoms the energy levels are insufficiently closely spaced, and in isolated molecules of this kind radiationless transitions to not occur. In impurity molecules radiationless transitions are always possible, because the overall spectrum of states of the system is quasi-continuous owing to the vibrational states of the solvent molecules. The rate of the radiationless transitions in the condensed phase may depend on the strength of the interaction of the vibrations of the impurity and solvent molecules, i.e. on the rate of vibrational relaxation[38-41]. Another cause of the existence of a continuous spectrum of states of the system is associated with the possible photochemical reactions. We shall consider these possibilities below and here we shall deal with radiationless transitions involving a large number of closely spaced discrete states. By definition, processes of this type do not lead (in the first stage) to chemical transformations in the system and are referred to as conversion processes.

The following instances of conversion are distinguished. If the transition is between electronically excited states with the same multiplicity, the corresponding process is called an internal conversion process. When the distance between the electronically excited states does not exceed ~1 eV, the rate of internal conversion is very high, amounting to $10^{11}-10^{12}$ s^{-1}.[24,27,42] In the vast majority of molecules, the distance between the neighbouring electronically excited states is ≤ 1 eV, and internal conversion processes in such systems are therefore very rapid. The azulene molecule[24], in which the distance between S_1 and S_2 states is ~1.7 eV, constitutes an exception. A process involving a change in the multiplicity of the states as a result of the transition is referred to as intercombination conversion (singlet–triplet or $S-T$ conversion). The rate of such conversion depends very strongly on the spin–orbital coupling of the states of the system and on its other characteristics[24,43,44]. The rate of $S-T$ conversion between $\pi\pi^*$ states of aromatic molecules is $10^{6}-10^{8}$ s^{-1}.[15] The rate of $S-T$ conversion between $\pi\pi^*$ and $n\pi^*$ states is very high (~$10^{10}-10^{11}$ s^{-1}) owing to the appreciable spin–orbital coupling between them[24,43]. The rate of $S-T$ conversion in aliphatic hydrocarbons should also be high[44]. If the system finds itself in the ground electronic state as a result of a radiationless transition, the process is called degradation of electronic energy. One should then distinguish two types: an internal degradation process (for example an S_1 S_0 transition in which the multiplicity of the states does not change) and an intercombination degradation process (involving a change in multiplicity, for example T_0 S_0).

In most molecules the S_1 state is located at a considerable distance from S_0 ($\geqslant$2.5 eV). Internal degradation in such systems is unlikely (its rate is $\sim 10^5$ s^{-1}) and cannot compete with the radiative decomposition of the S_1 state and the $S-T$ conversion[42,45]‡. As the energy of the first excited state of the system decreases, the role of the internal degradation process increases, and, in systems in which the energy of the first excited state is less than ~1.5 eV, it may become the main pathway to the deactivation of the excited state[42]. The rate of intercombination (T_0–S_0) degradation also depends very strongly on the energy of the excited state. The characteristic rate of this process in aromatic hydrocarbons at low temperatures is $\sim 10^{-1}$ s^{-1}. For molecules with the lowest $T_{n\pi^*}$ state, the probability of this process is much greater, and its rate is $\sim 10^2-10^4$ s^{-1}.[24,27] Electronically excited states may naturally decompose also via radiative channels. In allowed electronic transitions the rate of radiative decomposition is 10^8-10^9 s^{-1}. In symmetry-forbidden electronic transitions (the $\pi \to \pi^*$ electronic transition in benzene and the $n \to \pi^*$ transitions in carbonyl compounds) the rate of the radiative transition is somewhat lower and amounts to 10^5-10^6 s^{-1}. The probability of radiative transitions forbidden by multiplicity is much lower and their rate is $10^{-3}-10^3$ s^{-1}.[24,27]

IV. THE DISTRIBUTION OF VIBRATIONAL ENERGY IN THE INITIAL STATE

The rate and mode of decomposition of an electronically excited system depends significantly on the amount of vibrational energy and particularly on the nature of its distribution among the vibrational degrees of freedom. We are primarily interested in the possibility of the non-equilibrium excitation of the stretching R–H bond vibrations. The degree of excitation of these vibrations depends on the way in which the electronic state is "prepared".

Following optical excitation or excitation by electron impact, the probability of the excitation of vibrational states is determined by the corresponding Franck–Condon factor§. At low temperatures only those vibrations can be excited whose characteristics (frequency and/or equilibrium value of the normal coordinate) change in the electronic transition. In the majority of hydrocarbon molecules and their substituted derivatives the stretching C–H bond vibrations are not of this kind (see Section II), so that one cannot expect their significant excitation. The vibrational energy in such systems during the first instant after the electronic transition is concentrated in the stretching C–C bond vibrations or in the vibrations of a carbon–heteroatom bond.

The vibrational energy is distributed in a different manner if the electronic state $|f\rangle$ is formed as a result of internal conversion from a higher excited state $|i\rangle$. Because of the considerable anharmonicity of the R–H bond vibrations, their significant excitation in this process is to be expected. We shall demonstrate this in relation to a simple model. Suppose that the system has two vibrational degrees of freedoms, one of which is associated with the anharmonic R–H bond oscillator and the other with a vibration which can be described in terms of the harmonic approximation. (In aromatic hydrocarbons the C–C vibrations may be regarded as being of this kind with a high degree of accuracy.) The harmonic vibration is characterised by the difference Δ between the values of the equilibrium coordinate in the $|i\rangle$ and $|f\rangle$ states. For simplicity, we shall assume that the characteristics of the R–H bond vibrations in the $|i\rangle$ and $|f\rangle$ states are identical. The rate of internal conversion from the zero-point vibrational state corresponding to the electron energy level i, accompanied by the excitation of the nth vibration of the R–H bond and the mth harmonic vibration corresponding to the electron energy level f, is proportional to the square of the matrix element:

$$\frac{1}{\mu}\left\langle i\left|\frac{\partial}{\partial x}\right|f\right\rangle\left\langle 0\left|\frac{\partial}{\partial x}\right|n\right\rangle\langle 0|m\rangle. \tag{1}$$

Here μ and x are the reduced mass and the internal coordinate of the R–H vibration reckoned from the equilibrium value x_0; $|i\rangle$ and $|f\rangle$ are the electronic wave functions and $|0\rangle$, $|n\rangle$, and $|m\rangle$ are the vibrational wave functions. In order to calculate the value of the quantity defined by formula (1), one may employ the Morse functions for the R–H bond and the functions of the harmonic oscillator for the second vibration. The Morse potential is

$$U(x) = D(e^{-2\alpha x} - 2e^{-\alpha x}), \tag{2}$$

where D is the bond dissociation energy, $\alpha = \omega(\mu/2D)^{1/2}$, and ω is the zero-point vibration frequency of the oscillator. The wave functions of the discrete spectrum are of the following form[46]:

$$|n\rangle = \left[\frac{\alpha\Gamma(2s_0-n+1)}{n!\Gamma(2s_0-2n+1)\Gamma(2s_0-2n)}\right]^{1/2} y^{s_0-n}e^{-y/2}\cdot F(-n, 2s_0+1-2n, y), \tag{3}$$

where $s_0 = 2D/\omega - 1/2$, $0 \leqslant n < s_0$, $y = (2s_0+1)e^{\alpha x}$, $\Gamma(z)$ is the gamma-function, and $F(\alpha, \gamma, z)$ is a degenerate hypergeometric function. Using Eqn. (3), it is easy to obtain[47] an expression for the vibrational factor of the R–H bond in formula (1):

$$\left|\left\langle 0\left|\frac{\partial}{\partial x}\right|n\right\rangle\right|^2 = \frac{\alpha^2}{4}n!\,\frac{\Gamma(2s_0+1-n)(2s_0-2n)}{\Gamma(2s_0)}. \tag{4}$$

The calculation of the Franck–Condon factor $\langle 0|m\rangle$ with the functions of the harmonic oscillator presents no difficulty[48]:

$$|\langle 0|m\rangle|^2 = \frac{e^{-\eta}}{m!}\eta^m,\quad \eta = \frac{\Delta^2\mu'\omega'}{2}, \tag{5}$$

where ω' and μ' are the frequency and mass of the harmonic oscillator. The average values of the quantum number n are presented below as a function of the difference between the electronic energies ΔE_{if} of the i and f electron energy levels and the parameter s_0:

ΔE_{if}, eV	0.5 eV	1 eV	1.5 eV	2 eV
$s_0=15$	0.1	0.8	3.6	4.6
$s_0=30$	0.06	0.5	0.96	2.1

The following values of the parameters were selected: $\omega = 3000$ cm^{-1}, $\omega' = 1500$ cm^{-1}, and $\eta = 1$. Evidently the probability of the excitation of the R–H bond vibrations in a non-adiabatic transition increases with increasing anharmonicity of the vibrations (with decrease of the bond energy) and with increase of ΔE_{if}. For typical values $\Delta E_{if} \simeq 1-2$ eV, the R–H bond vibrations are significantly excited. This result may be obtained only when account

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‡ This also show that decomposition of the majority of molecules cannot proceed via the mechanism involving the concentration of vibrational energy by fluctuations.

§ It is postulated that the corresponding electronic transition is symmetry-allowed.

is taken of the anharmonicity of the R–H vibrations, since in terms of the harmonic approximation the R–H vibrations with $n > 1$ are not excited at all in our model.

It is noteworthy that the above result is comparatively new, because it had been assumed earlier that in the internal conversion the energy is transmitted more or less uniformly to all the vibrational modes of the system. The average energy of the ν-mode is then determined (in terms of the harmonic approximation) by the parameter Δ_ν, the vibration frequencies ω_ν, and the amount of energy converted ΔE_{if}.[49] For higher and lower values of ΔE_{if}, the high-frequency and low-frequency vibrations are excited preferentially. The vibrational energy is always delocalised over the molecule in the harmonic approximation. As shown above, allowance for the anharmonicity of the vibrations leads to the possibility of the localisation of the vibrational energy in an individual bond.

An excited state may arise also as a result of intercombination conversion, which occurs under the influence of the spin–orbital interaction and (in terms of second-order perturbation theory) a non-adiabatic interaction. For intense spin-orbital interaction (~10 cm^{-1}), which depends little on the internuclear distances, the interconversion does not entail a significant excitation of the C–H bond vibrations. An example is provided by the transitions between the $n\pi^*$, and $\pi\pi^*$ states of different multiplicity. If the spin–orbital coupling is weak (~0.1 cm^{-1} for aromatic hydrocarbon molecules), terms describing the contribution of the non-adiabatic interaction may contribute significantly to the probability of the transition. In this case the excitation of the C–H vibrations is more likely in a radiationless transition.

V. NON-ADIABATIC DECOMPOSITION

A molecular system in the adiabatic vibronic state $|i\{n\}\rangle$ has a finite probability of a transition under the influence of the non-adiabatic operator to a continuum of $|f\{s\}\rangle$ states, provided that their multiplicities are identical. $\{n\}$ and $\{s\}$ are understood as sets of indices characterising the wave functions of the nuclei $|\{n\}\rangle$ and $|\{s\}\rangle$. The possibility of a continuous spectrum of $|f\{s\}\rangle$ states in any electronic state is determined by the finite value of the bond energy of the atoms in the system. In the region of energies exceeding the dissociation energy of any of the bonds the energy spectrum is continuous and the corresponding wave functions describe the motion of the decomposition products moving apart to infinity. The transitions of the system to such states will be considered here.

The $|i\{n\}\rangle$ state should be understood as an excited vibronic state of the R–H system. The $|f\{s\}\rangle$ states correspond to a continuous energy spectrum of the R$^\cdot$ + H system. The energy of the $|i\{n\}\rangle$ state should naturally exceed the dissociation energy of the R–H bond in the $|f\rangle$ state. The electronic wave functions $|i\rangle$ and $|f\rangle$ for molecules may be calculated by one of the methods of quantum chemistry; we shall make use of the wave functions found by the LCAO-MO method. The situation is somewhat more complex for wave functions describing the motion of nuclei.

The vibrational wave functions $|\{n\}\rangle$ are products of the functions of normal oscillators of the system. The $|\{s\}\rangle$ wave function can also be represented as the product of the function describing the relative motion of the R and H fragments and the vibrational wave functions of the R fragment. The forms of the normal coordinates in the $|i\rangle$ and $|f\rangle$ states are evidently not the same and the above representation of the $|\{n\}\rangle$ and $|\{s\}\rangle$ functions is unsuitable for the calculation of the rates of transition. It is seen that, when the dispersions of the vibration frequencies of the R–H bonds are neglected, the $|\{n\}\rangle$ and $|\{s\}\rangle$ functions are products of the vibrational functions of individual R–H bonds and the functions of the normal oscillators of the remainder of the molecule. The dispersion of the frequencies of the C–H(R–H) bond vibrations is small (~100 cm^{-1}) compared with the vibration frequency (~3000 cm^{-1}) and particularly the bond dissociation energy; for this reason, its neglect leads to very small changes in the decomposition probability. This is even more valid for anharmonic oscillators, because allowance for anharmonicity leads to an effective decrease of the intensity of their interaction[50].

We shall employ the Morse functions as the vibrational wave functions of R–H bonds. The $|\{n\}\rangle$ wave function is the product of the $|n_\nu\rangle$ wave functions, the discrete states of the Morse potential for individual R–H bonds, and the functions of the normal oscillators in the remainder of the molecule. The wave function of the final state is the product of the wave function $|s\rangle$ of the continuous spectrum of the Morse potential, which describes the motion of the eliminated hydrogen atom, and of the wave functions $|n'_\nu\rangle$ of the rest of the system, including the remaining R–H bonds. The vibrational quantum numbers n'_ν may differ from the initial numbers n_ν. The rate of the transition $|i\{n\}\rangle$ $|f\{s\}\rangle$ under the influence of the adiabatic operator is described by the following expression in terms of the first-order perturbation theory[9]¶:

$$k = 2\pi \left| \frac{1}{\mu} \left\langle i \left| \frac{\partial}{\partial x} \right| f \right\rangle_{x=0} \left\langle \{n\} \left| \frac{\partial}{\partial x} \right| \{s\} \right\rangle \right|^2, \ (\hbar = 1), \tag{6}$$

The vibrational factor defined by Eqn.(6) is

$$\left\langle \{n\} \left| \frac{\partial}{\partial x} \right| \{s\} \right\rangle = \left\langle n \left| \frac{\partial}{\partial x} \right| s \right\rangle \prod_\nu \langle n_\nu | n'_\nu \rangle, \tag{7}$$

where the product of the Franck–Condon factors $\langle n_\nu | n'_\nu \rangle$ is evaluated with respect to all the normal oscillators and bonds except the bond undergoing dissociation. In order to obtain the total probability of the abstraction of any hydrogen atom (per unit time), the expression for k must be summed with respect to finite vibrational states of the fragment R and with respect to all the R–H bonds. Furthermore, Eqn.(6) must be averaged with respect to the initial vibrational distribution.

The wave functions of the continuous spectrum of the Morse potential are of the form

$$|s\rangle = \frac{|\Gamma(-s_0 + is)|}{|\Gamma(2is)|\,(2\pi v)^{1/2}}\, y^{-1/2} W_{s_0+1/2,\, is}(y), \tag{8}$$

where $v = (2E/\mu)^{1/2} = \alpha s/\mu$, $s = (2\mu E)^{1/2}/\alpha$, and $W_{s_0+1/2,is}(y)$ is the Whittacker function. Function (8) is normalised with respect to the delta-function of energy E, which is reckoned from the dissociation energy L.

¶ It is noteworthy that terms containing derivatives with respect to other coordinates of the molecule may contribute to k. Since the difference between the bond lengths in the $|i\rangle$ and $|f\rangle$ states is small (see Section II) and the integral $\langle n|s\rangle$ for low values of n is therefore close to zero, these terms may be neglected. This applies also to the non-adiabatic interaction term containing second derivatives of the electronic functions with respect to internuclear coordinates. The expression for k is quoted in terms of atomic units.

The Franck–Condon factors reach their maximum value for $n_\nu \simeq n'_\nu$ under the conditions of a small change in the equilibrium value of the coordinate of the oscillator (Δ_ν). When $n = 0$ and for $n'_\nu \ll s_{0\nu}$, when the harmonic approximation is valid, we have[42,48]

$$|\langle 0 | n'_\nu \rangle|^2 = e^{-\eta_\nu} \eta_\nu^{n'_\nu} (n'_\nu!)^{-1}, \quad \eta_\nu = \Delta_\nu^2 \mu_\nu \omega_\nu / 2. \tag{9}$$

Calculation of the integral $\left\langle n \left| \frac{\partial}{\partial x} \right| s \right\rangle$ for an unchanged length ($\Delta = 0$) and vibration frequency of the R–H bond† in the $|i\rangle$ and $|f\rangle$ states gives[47]

$$\left|\left\langle n \left| \frac{\partial}{\partial x} \right| s \right\rangle\right| = S_{ns} = \frac{\mu (2s_0 - 2n)}{8\pi n! s} \frac{|\Gamma(-s_0 + is)|^2 \cdot |\Gamma(s_0 + 1 + is)|^4}{\Gamma(2s_0 + 1 - n) \cdot |\Gamma(2is)|^2}. \tag{10}$$

The integral $\left\langle n \left| \frac{\partial}{\partial x} \right| s \right\rangle$ may be also calculated analytically for $\Delta \neq 0$. When $n = 0$, we have

$$\left|\left\langle 0 \left| \frac{\partial}{\partial x} \right| s \right\rangle\right|^2 = S_{0s} \left[\xi^{s_0+1} F\left(s_0 + 1 + is, s_0 + 1 - is; 1; \frac{1-\xi}{2}\right) + \right.$$
$$\left. + s_0 (\xi - 1) \xi^{s_0} F\left(s_0 + 1 + is, s_0 + 1 - is; 2; \frac{1-\xi}{2}\right)\right]^2, \tag{11}$$

where $\xi = e^{\alpha\Delta}$ and $F(\alpha, \beta; \gamma; z)$ is a hypergeometric function. The expressions for the quantities $\left\langle n \left| \frac{\partial}{\partial x} \right| s \right\rangle$ when $n \neq 0$ can also be represented by the product of S_{ns} and a function $\Phi(s_0, s, n, \Delta)$, which is not quoted here because of its cumbersome form. The fundamental dependence of the factor $\left|\left\langle n \left| \frac{\partial}{\partial x} \right| s \right\rangle\right|^2$ on n is contained in the multiplier S_{ns}.

The expression for S_{ns} when $s_0 \gg 1$, $n \ll s_0$, and $s \geqslant 1$ can be greatly simplified if the asymptotic expression for the gamma-function is used[47]:

$$S_{ns} \simeq \frac{\pi^{1/2} \mu}{n! 2^{2s_0}} s_0^{3/2} (2s_0)^n (1 + s^2/s_0^2)^{s_0+1/2} \exp\left(-2s \arctan \frac{s}{s_0}\right). \tag{12}$$

If the decomposition takes place in the nth vibrational state of the bond undergoing dissociation and all the remaining numbers $n_\nu = 0$, one can write

$$k = \frac{2\pi^{3/2}}{\mu} |\beta|^2 F \prod_\nu \eta_\nu^{n'_\nu} e^{-\eta_\nu} (n'_\nu!)^{-1}, \tag{13}$$

where $\beta = \left\langle i \left| \frac{\partial}{\partial x} \right| f \right\rangle_{x=0}$ and the function

$$F = \pi^{-1/2} \mu^{-1} \left|\left\langle n \left| \frac{\partial}{\partial x} \right| s \right\rangle\right|^2.$$

For the majority of molecules, the parameter η_ν is non-zero only in the case of certain oscillators; under these conditions, its characteristic value is close to unity[48,51]. In this instance the multipliers with $n'_\nu \leqslant 1$ make the maximum contribution to Eqn. (13). Hence it follows that $\prod_\nu \eta_\nu^{n'_\nu} e^{-\eta_\nu} (n'_\nu!)^{-1} \sim 0.1$ and the fragment R can acquire a small amount of vibrational energy during the decomposition process, provided that this is allowed by energy factors. The fundamental dependence of k on the molecular parameters is contained in the multiplier F.

Fig. 1 illustrates the variation of F with s_0 for $n = \Delta = 0$; evidently F decreases sharply with increase of s_0. The dependence of F of the parameter s is illustrated in Fig. 2. When $s = 0$, we have $F = 0$, but, when $s \simeq 0.5$ ($E \simeq 10^2$ cm^{-1}), F already reaches a maximum and then slowly decreases. Fig. 3 illustrates the variation of F with the length of the bond undergoing dissociation in the excited state; evidently the decomposition probability increases as the bond length is diminished. With increase of bond length, F initially decreases somewhat and then assumes a value virtually equal to that corresponding to $\Delta = 0$.

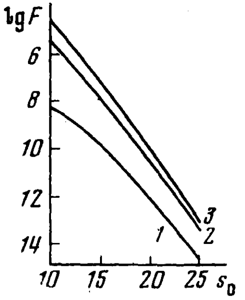

Figure 1. Dependence of the factor F on the parameter s_0 ($\Delta = 0$, $n = 0$); s: 1) 10; 2) 5; 3) 1.

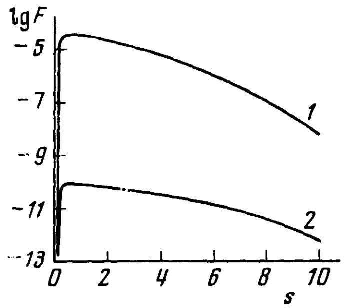

Figure 2. Dependence of the factor F on the parameter s ($\Delta = 0$, $n = 0$); s_0: 1) 10; 2) 20.

It follows from Eqn. (12) that the factor F increases very rapidly with increase of the vibration quantum number of the R–H oscillator in the initial state. Since $2s_0 \geqslant 10$, the excitation of the R–H bond vibrations leads to an increase in the probability of dissociation by more than an order of magnitude for each vibrational quantum.

In the Appendix to the present review it is shown that in many interesting cases $|\beta|^2 \simeq 2$ a.u. The constant for the elimination of a hydrogen atom is then given by

$$k \simeq 10^{14} \cdot F \ (\text{s}^{-1}). \tag{14}$$

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† We may note that the value of $\left\langle n \left| \frac{\partial}{\partial x} \right| s \right\rangle$ for $n \ll s_0$ (this is the case which we are in fact considering) is independent of the bond dissociation energy in the excited state, because the functions $|n\rangle$ are converted into the function of the harmonic oscillator when $n \ll s_0$.

The results of the calculation by Eqn. (14) of the rate constants for the decomposition of molecular systems with elimination of a hydrogen atom for different R–H bond energies are presented below:

D, eV	1.5	2.0	2.5	3.0	3.5	4.0	4.5
s_0	7.6	10.3	13.0	15.7	18.4	21.1	23.8
lg k, (s^{-1})	10.7	9.3	7.8	6.3	4.8	3.3	1.7

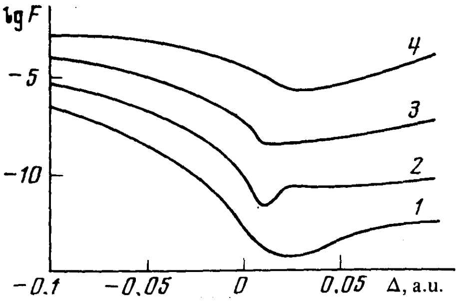

Figure 3. Dependence of the factor F on the parameter Δ ($s = 1$, $n = 0$); s_0: 1) 25; 2) 20; 3) 15; 4) 10.

In all cases it was assumed that $\omega = 3000$ cm^{-1}, $s = 1$, $\Delta = 0$, and $n = 0$. Several important conclusions follow from the above data: (1) the probability of the elimination of a hydrogen atom via a non-adiabatic mechanism from electronically excited molecular systems, for which $D \simeq 4-4.5$ eV (the majority of hydrocarbon molecules), is very low when $n \simeq 0$, and the quantum yield of the dissociation of the R–H bonds cannot exceed $\sim 10^{-3}$. (2) With decrease of the bond energy to 2.5–3.5 eV, the values of k become comparable to the rates of decomposition of the lowest singlet states of the majority of molecules, and the quantum yield of the decomposition in such systems may become appreciable. (3) If the bond energy becomes $\lesssim 2$ eV (paraffin radical-cations), the values of k exceed not only the rate constants for the radiative decomposition, but also the rate constants for internal conversion and vibrational relaxation. In this situation the quantum yield for the elimination of a hydrogen atom approaches unity.

$|\beta|^2 \simeq 2$ a.u. has been estimated for the case where the R–H bond is located in the part of the molecule where the excitation is localised (for example, a C–H bond of benzene). With increase of the distance R between the bond undergoing dissociation and the region where the wave function of the excited state is appreciably different from zero, the matrix element diminishes as R^{-2}. Therefore the constant k should be estimated, for example, in the case of the toluene molecule, from the formula $k \simeq$ $k \simeq 10^{12} F$. This must be taken into account when specific systems are considered.

It follows from the results presented that, other conditions being equal, the weakest R–H bond in the molecule will be preferentially dissociated. In most instances this has been observed experimentally, and henceforth we shall concentrate attention (without additional stipulations) on the description of the dissociation of the weakest R–H bond. One should bear in mind that the energy of the R–H bonds in excited electronic states is frequently smaller than in the ground state. Hence it follows that the probability of decomposition in the highest electronically excited states with formation of the fragment R in an electronically excited state may be much greater than the probability of the process involving the formation of the fragment R in the ground state. This decomposition pathway ($\overset{*}{M} \rightarrow \overset{*}{R} + H$) can be significant in the gas phase, but not in the condensed phase, since the lifetime of the highly excited states of molecular systems is very short in the condensed phase.

VI. PREDISSOCIATIVE DECOMPOSITION

We noted above (Section II) that, owing to the delocalisation of the electronic excitation over the molecular system, there are no significant changes in bond lengths if the number of bonds is large. However, the delocalisation may be infringed if the length of one or several equivalent bonds changes. In this situation a level may arise in the system with the localisation of the excitation energy at an individual bond [30,52], which leads to its dissociation. We shall examine the conditions for the appearance of such a level in a simple model of N equivalent two-electron bonds, weakly interacting with one another. Such are the C–H bonds of the majority of molecules.

The wave function of the ground state of the system can be described in the following form in terms of the zeroth approximation:

$$\Psi_0 = \hat{A} \prod_{n=1}^{N} \varphi_n^0 (R_n, \mathbf{r}_{1n}, \mathbf{r}_{2n}), \tag{15}$$

where $\hat{A}$ is the antisymmetrisation operator and $\varphi_n^0 (R_n, \mathbf{r}_{1n}, \mathbf{r}_{2n})$ is the wave function of the ground state of the nth bond, which depends on its length R_n and the electron coordinates $\mathbf{r}_{1n}$ and $\mathbf{r}_{2n}$. The dependence of the energy of each bond on R_n has the form of the $E^0(R_n)$ Morse curve and the energy of the entire system is

$$\sum_{n=1}^{N} E^0(R_n)$$

reaching a minimum for the equilibrium values of $R_n = R_n^0$.

The wave function of the excited state of the system can be expressed as the product of the wave functions $\varphi^1(R_n, \mathbf{r}_{1n}, \mathbf{r}_{2n})$ of the excited states of individual bonds (the strong bond approximation):

$$\Psi_j = \sum_{n=1}^{N} c_{jn} \hat{A} \varphi_n^1 (R_n, \mathbf{r}_{1n}, \mathbf{r}_{2n}) \prod_{\substack{n' \neq n \\ n'=1}}^{N} \varphi_{n'}^0 (R_{n'}, \mathbf{r}_{1n'}, \mathbf{r}_{2n'}). \tag{16}$$

The dependence of the energy $E^1(R_n)$ of an individual bond in the excited state on its length naturally differs from the function $E^0(R_n)$, which actually makes possible the localisation of the excitation energy at an individual bond. Using the variational principle for the energy, we obtain a system of equations defining E_j and c_{nj}:

$$\left[\sum_{\substack{n'=1 \\ n' \neq n}}^{N} E^0(R_{n'}) + E^1(R_n)\right] c_{nj} + \beta (c_{n+1,j} + c_{n-1,j}) = E_j c_{nj}, \tag{17}$$

where β is the resonance integral for the interaction of adjacent bonds.

We shall consider the dependence of wave functions (16) on the length of one of the bonds. If all the R_n are equal to their equilibrium values R_n^0, then E_j and c_{nj} are defined by the expression

$$E_j = (N-1)E^0(R_n^0) + E^1(R_n^0) + 2\beta\cos\frac{j\pi}{N+1},$$
$$c_{nj} = \sqrt{\frac{2}{N+1}}\sin\frac{jn\pi}{N+1}, \quad 1 \leqslant j \leqslant N. \tag{18}$$

In this case excitation delocalised over the entire system corresponds to each value of j. The change in bond order on excitation amounts to $\sim N^{-1}$, which is responsible for the small change in the $E_j(R_n)$ relation in the vicinity of R_n^0 when $N \gg 1$ compared with the $E^0(R_n)$ relation.

The change in the length of one of the bonds alters the matrix element in Eqn. (17) corresponding to this bond. The remaining matrix elements may then be regarded as invariant. The solution of this type of system of equations has been considered[53] and it has been shown that the $(N-1)$th solution again corresponds to the delocalisation of the excitation over the system and is described by an equation of type (18). However, one of the levels has a wave function (for $N \to \infty$) which decreases exponentially with increase of the distance from the selected bond n_0:

$$c_n = \exp[-|n_0 - n|\varkappa(R_{n_0})],$$
$$\sinh\varkappa(R_{n_0}) = [E^0(R_{n_0}) + E^1(R_{n_0}^0) - E^0(R_{n_0}^0) - E^1(R_{n_0})]/2\beta. \tag{19}$$

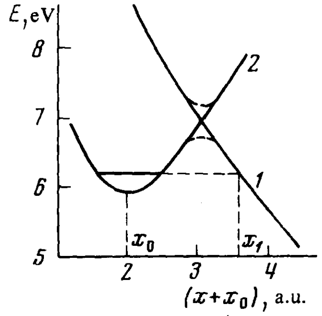

Figure 4. The energy levels of the localised (triplet) (curve 1) and delocalised (curve 2) states as a function of the C–H bond length.

It is seen from Eqn. (19) that the excitation may be localised if $\varkappa(R_{n_0}) \neq 0$. This situation is observed when the excitation energy decreases with increase in bond length, which implies that the excitation may be localised when the electron energy level of the excited state of an isolated bond is of the repulsive type. The energy of the system in state (19) is described by a curve with an activation barrier (Fig. 4) and the elimination of a hydrogen atom under the conditions of low excitation energies corresponds to a transition through the barrier.

In the region of excitation energies of hydrocarbons and their substituted derivatives not exceeding ~10 eV, the repulsive electron energy level of the C–H bond is of the triplet type[5]. The functions corresponding to this level describe the relative motion of the hydrogen atom and the radical in the ground electronic state moving apart to infinity.

The problem of the calculation of the rate of decomposition of molecular systems via a mechanism involving the localisation of the electronic excitation energy at the bond undergoing dissociation (which we shall call the predissociative mechanism) has already been examined[5,6]. It has been shown that the bond dissociation corresponds to a transition of a hydrogen atom from the energy level of a binding (delocalised) state to the repulsive energy level of the state where the electronic excitation is localised at an individual bond. Fig. 4 illustrates cross-sections of the potential surfaces for these two states as a function of the coordinate of the stretching vibrations of the R–H bond.

If the initial (delocalised) state is of the triplet type, then the localisation of the energy at an individual bond is due to an electron–electron (exchange) interaction. For a singlet initial state, the transition to a repulsive energy level can occur only under the influence of a relatively weak (see below) spin–orbital interaction. Hence follows immediately the important conclusion that the decomposition with elimination of a hydrogen atom can occur with a high probability only in triplet states.

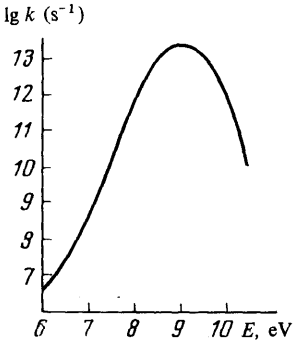

Figure 5. Dependence of the rate constant for the predissociative elimination of a hydrogen atom on the excitation energy.

Evidently the probability of the decomposition will depend on the relative positions of the energy levels of the initial and final states. As shown in Section II, the position of the energy level of the initial state for fairly complex molecules is determined solely by the electronic excitation energy. The position of the repulsive energy level depends on the bond dissociation energy and the energy of the exchange repulsion of the electron of hydrogen from the unpaired electron of the radical. (The remaining interactions are naturally also reflected in the position of the repulsive energy level, but their extent changes little from molecule to molecule.) The C–H bond dissociation energy is reduced in those cases where the unpaired p-electron is delocalised in the radical formed. The greater the degree of delocalisation of the unpaired electron, the smaller the energy of the exchange repulsion between hydrogen and the radical. Thus, as a result of the decreased bond energy, the repulsive energy level is lowered and the dissociation probability is a maximum for the weakest of the R–H bonds. This conclusion is therefore common to non-adiabatic and predissociative mechanisms.

The use of the formula of the first-order perturbation theory to calculate the rate constant for predissociation with rupture of the R–H bond yields the expression

$$k = 2\pi|\beta|^2|\langle n\}|\{s\}\rangle|^2, \tag{20}$$

where β is the matrix element of the electron–electron (spin–orbital) interaction between the initial and final states and $|\{n\}\rangle$ and $|\{s\}\rangle$ designate, as before, the wave functions of the nuclei in the initial and final states. Owing to the weak dependence (for slight displacements of the nuclei) of the operators of the electron–electron and spin–orbital interactions, Eqn.(20) includes the factor governing the overlapping of the nuclear functions of the initial and final states. It is noteworthy that Eqn.(20) is applicable in the region where the potential curves of the localised and delocalised states differ little from the true curve plotted taking into account their interaction. In the region of the intersection of the potential curves Eqn.(20) yields only an approximate estimate, somewhat smaller than the exact value. This region diminishes with increase in the number of bonds in the molecule.

The wave functions $|\{n\}\rangle$ are chosen in the same form as in the description of the non-adiabatic decomposition. Since the decomposition takes place, as a rule, in vibrational states with small quantum numbers ($n \lesssim 3$), the harmonic oscillator function may be adopted as the vibrational wave functions. This makes it possible to obtain, without loss of accuracy, an expression for k in a form suitable for calculation.

The wave functions $|\{s\}\rangle$ have a more complex form than those described in Section V. The point is that the potential surface of the final state is of the repulsive type not only in the direction of the stretching vibrations of the bond undergoing dissociation, but also in the direction of its deformation vibrations. Depending on the stretching vibration coordinate x, a function Ax, where A is the slope of the plot of the repulsive energy level, may be fitted to the potential surface. The parabolae By^2, where $B < 0$, may be fitted to the dependence of the repulsive electron energy level on the deformation displacements of the hydrogen atom[6]. Accordingly, the products of the Airy function[46] and two Whittacker functions[47] are used as the functions of the final state of the bond being dissociated. For the remaining bonds, the harmonic oscillator functions are used.

The calculations[6] yield an expression for k:

$$k = \frac{\sqrt{3}\pi|\beta|^2}{2}\prod_{\nu}\frac{\eta_\nu^{n'_\nu}e^{-\eta_\nu}}{n'_\nu!}\int_{-\infty}^{+\infty}\cosh^{-1}\left(\frac{z\pi}{2}\right)e^{\frac{\pi z}{6}}S^2\left(\delta-\frac{\omega_2}{A}+\frac{z\omega_2}{\sqrt{3}A}\right)dz, \tag{21}$$

where $\delta = x_1 - x_0 = (E_0 - E)/A$, where E_0 is the energy of the repulsive triplet level at the point of equilibrium (in the ground state) of the R–H bond, E is the energy of the initial state after the subtraction of the energy transformed into the energy of the vibrational excitation of the fragment R, and ω_2 is the deformation vibration frequency of the R–H bond. E_0 in most cases exceeds significantly (by 2–4 eV) the energy of the R–H bond. The remaining notation is the same as in Eqn.(9). The function $S(y)$ is defined by

$$S(y) = \left(\frac{2^{10}\mu}{A^2\pi^3\omega_1^3}\right)^{1/12}(2^n n!)^{-1/2}\left[\frac{\partial^n}{\partial t^n}S(t)\right]_{t=0},$$

$$S(t) = \exp\left(t^3-\frac{c^3}{\alpha^3}t+\frac{a}{2}y+\frac{b}{2}\right)\Phi\left(yc+d-\frac{2c}{\alpha}t\right), \tag{22}$$

where μ is the reduced mass, ω_1 the frequency of the stretching vibrations of the R–H bond, n the vibrational quantum number characterising the excitation of the stretching vibrations of the R–H bonds in the initial electronic state, $\alpha = \sqrt{\mu\omega_1}$, $c = (2\mu A)^{1/3}$, $a = c^3/\alpha^2$, $b = c^6/6\alpha^6$, $a = c^4/4\alpha^4$, and $\Phi(z)$ is the Airy function. In order to obtain the complete rate of elimination of hydrogen atoms, Eqn.(21) must be averaged with respect to the initial vibrational (electronic) states and summed with respect to the possible final states.

For rough estimates, the following formula may be used to calculate k:[5,54]

$$k = \frac{2\pi}{A}|\beta|^2\prod_{\nu}\frac{\eta_\nu^{n'_\nu}e^{-\eta_\nu}}{n'_\nu!}\Omega_n^2(\delta), \tag{23}$$

where $\Omega_n(\delta)$ is the function of the harmonic (anharmonic) oscillator of the stretching R–H bond vibration. The wave function $\Omega_0(\delta)$ is of the form

$$\Omega_0(\delta) = \left(\frac{\mu\omega_1}{\pi}\right)^{1/4}\exp(-\mu\omega_1\delta^2/2). \tag{24}$$

Hence it is seen that, when the parameter δ (i.e. the excitation energy) is altered, k passes through a maximum, where $E = E_0$ and $\delta = 0$. A similar variation of k is obtained when Eqn.(22) is used.

The parameter β has been estimated[5,55,56]. In the case of decomposition in triplet $\pi\pi^*$ states of aromatic (unsubstituted) hydrocarbons β is defined by the expression $\beta \simeq 10^{-2}N^{-1}$ a.u., where N is the number of carbon atoms in the molecule. Hence it is seen that the probability of the elimination of a hydrogen atom decreases as N^{-1}. For the lowest triplet states of aromatic hydrocarbons, β is defined by the expression $\beta \simeq 10^{-2}N^{-1/2}$ a.u., so that the probability of the decomposition of the molecule with elimination of a hydrogen atom is independent of molecular size for aliphatic hydrocarbons. A similar situation obtains also for the $n\sigma^*$ states of substituted aliphatic hydrocarbons.

Bearing in mind that, as in Section V, the quantity

$\prod_{\nu}\exp(-\eta_\nu)\eta_\nu^{n_\nu}(n_\nu'!)^{-1} \simeq 0.1$ and using $\beta = 10^{-2}$ a.u., we

obtain the following expression for k:

$$k(\mathrm{s}^{-1}) \simeq 10^{12}\int_{-\infty}^{\infty}\cosh^{-1}\left(\frac{\pi z}{2}\right)\exp\left(\frac{\pi z}{6}\right)S_n^2\left(\delta-\frac{\omega^2}{A}+\frac{\omega_2 z}{\sqrt{3}A}\right)dz. \tag{25}$$

The evaluation of the integral in Eqn.(25) does not present difficulties in most cases[6]. Since $n'_\nu \lesssim 1$, the vibrational energy of the fragment R cannot be large. Fig. 5 illustrates the variation of k with the parameter E calculated by Eqn.(25) for the following values of other parameters: $\omega_1 = 3000$ cm^{-1}, $\omega_2 = 1100$ cm^{-1}, $A = 0.1$ a.u., $E_0 = 9$ eV, and $n = 0$.

The $k(E)$ relation for decomposition in excited singlet states is of the same type. Since β for the dissociation of R–H bonds does not exceed several cm^{-1} in this instance[44], the values of k are reduced compared with decomposition in triplet states by 6–7 orders of magnitude. This means that the rate of decomposition in singlet states cannot be significant even for high excitation energies.

A few words may be said about the temperature dependence of the rate of decomposition. As already mentioned at the beginning of this Section, when the excitation energies do not exceed E_0, the elimination of a hydrogen atom is a process involving penetration through an activation barrier. k is independent of temperature at low values of the latter, in the present instance when $T < \omega k_B^{-1}$, where k_B is the Boltzmann constant, and ω is the C–H bond vibration frequency. Since $\omega \gtrsim 1000$ cm^{-1}, k acquires its low-temperature (quantum) value already at

300–400°C. At higher temperatures k increases with increase of T.

If the lowest triplet state of the molecule is located in the region of the maximum on the $k(E)$ curve, the molecule decomposes with a high probability in this state and the process involves elimination of a hydrogen atom. (We do not take into account other possible photochemical reactions.) With decrease of the energy of the lowest triplet state, the probability of decomposition diminishes. In this case, when the energy of the lowest triplet state is smaller than the bond dissociation energy, the elimination of a hydrogen atom is possible only in the highest excited triplet states. Internal conversion, which in most cases is very rapid and suppresses the predissociation process, competes with the above process. In certain molecules the rate of internal conversion may be reduced owing to the characteristics of their structure (see Section IX).

One should bear in mind that, for molecules with a small (smaller than E_0) ionisation potential, the maximum in the function $k(E)$ is in the region of the ionised states of the molecule. The excited (superexcited or autoionisation) states ionise rapidly in this situation ($10^{13}-10^{15}$ s^{-1}). This pathway to the decomposition of molecules, which does not itself lead to chemical changes in the molecule, constitutes an additional factor increasing the stability of molecules with respect to the elimination of a hydrogen atom. We may note that in the condensed phase the ionisation potential is lower than its value in the gas phase[57,58].

The stability of the molecules (in relation to the elimination of a hydrogen atom) is thus related to the positions of the triplet states, the ionisation potential, and the probability of deactivation processes‡. When specific systems are considered, one must of course bear in mind also the efficiency of the formation of triplet states. All the foregoing considerations are applicable (except for the names of the states) also to radicals and radical-cations. For this reason and also because the energy of the excited states of these systems is usually low[3,22,59,60] and the predissociative mechanism cannot therefore make a large contribution, the latter will not be discussed in detail.

VII. THE ISOTOPE EFFECT

The isotope effect in elimination reactions, which is defined as the ratio of the rate constants for the elimination of H and D atoms, can be used to test theoretical ideas about the process mechanism. Since the quantum yield is the main experimental characteristic of photochemical reactions, we shall consider briefly the conditions whose fulfilment is necessary for the observation of the influence of the isotope effect on the yield of the reaction[56].

We shall designate the rate constant for the dissociation of the C–H bond by k_H and that for the dissociation of the C–D bond by k_D. Suppose that the rate of deactivation of the excited states by all the pathways except decomposition is characterised by the constants k and k' respectively in the case of light and deuterated molecules. Then the quantum yield of the dissociation of the C–H and C–D bonds can be formulated thus:

$$Q_H = \frac{k_H}{k_H + k}, \quad Q_D = \frac{k_D}{k_D + k'}.$$

For low irradiation times, the rate of accumulation of products (the yield) is proportional to the quantum yield of the decomposition and we have for the ratio of the rates of accumulation of the light and deuterated molecules during photolysis

$$\frac{u_H}{u_D} = \frac{k_H}{k_D} \cdot \frac{k_D + k'}{k_H + k}. \tag{26}$$

If $k = k'$, $k' \gg k_D$, and $k \gg k_H$, then $u_H/u_D = k_H/k_D$, so that only in this case is the experimental ratio of the rates of accumulation of products equal to the ratio of the bond dissociation rate constants. Since the inequality $k_D + k' < k_H + k$ always holds, the ratio u_H/u_D gives the lower limit of the true value of the isotope effect.

It follows from the results presented in Sections V and VI that the isotope effect and its dependence on the excitation energy differ for the non-adiabatic and predissociative mechanisms. We shall consider initially the predissociative decomposition mechanism. The replacement of a hydrogen atom by a deuterium atom leads to an increase of μ by a factor of ~ 2 and to a decrease of ω_1 by a factor of $\sim\sqrt{2}$. It is readily seen that, for all the values of the parameter E, the change in the transition energies of the molecule on deuteriation may be neglected in the calculation of k_H/k_D without appreciable error. We then obtain from Eqn. (24)

$$\frac{k_H}{k_D} = 2^{-1/4} \exp\left[\mu\omega_1\delta^2 (\sqrt{2}-1)\right] = 2^{-1/4} \exp\left[\frac{\mu\omega_1}{A^2}(E - E_0)^2 (\sqrt{2}-1)\right]. \tag{27}$$

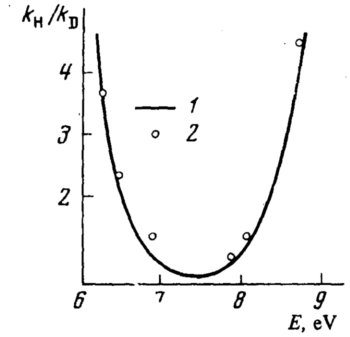

Figure 6. The isotope effect in the predissociative elimination of a hydrogen atom: 1) theory; 2) experiment[61].

Hence it is seen that the isotope effect exhibits a characteristic dependence on the excitation energy. For low excitation energies ($E < E_0$), the isotope effect is large. It decreases with increase of excitation energy, passes through a minimum when $E = E_0$, and then rises to high values again. Eqn. (27) refers to the decomposition in the zero-point vibrational state. A similar although more complex dependence has been observed also for the decomposition in vibrational excited states.

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‡ Studies have been published recently[94,95] in which it has been shown that the decomposition of hydrocarbon molecules in T states takes place with elimination of a hydrogen atom via a predissociative mechanism.

The dependence of the isotope effect on the excitation energy has been studied experimentally[61] in relation to the two-quantum decomposition of triphenylmethane with dissociation of the central C–H bond. The triphenylmethane molecule satisfies the requirements specified at the beginning of this Section, and the measured ratio $u_H/u_D = k_H/k_D$.[56]

Fig. 6 presents the dependence of k_H/k_D on E, calculated by Eqn. (21), together with the experimental values[61]. The only parameter which was varied in order to obtain the best agreement with experiment was the energy of the vertical transition to the repulsive E_0 energy level. Thus $E_0 = 7.4$ eV was found. Evidently not only qualitative but also quantitative agreement between the theoretical and experimental variations of k_H/k_D with E is observed. This result constitutes a convincing demonstration of the predissociative mechanism for the decomposition of electronically excited polyatomic molecules with elimination of a hydrogen atom. We shall present below (Section VIII) yet another experimental result of this kind.

The isotope effect in a non-adiabatic elimination reaction depends very strongly on the bond energy. The replacement of a hydrogen atom by a deuterium atom leads to an increase of the parameter s_0 in Eqn. (10) by a factor of $\sim\sqrt{2}$. The data in Section V show that the rate of decomposition decreases almost by an order of magnitude for bond energies $\lesssim 2$ eV and by more than an order of magnitude for higher bond energies. Unfortunately no experimental data are at present available for the isotope effect in a non-adiabatic elimination reaction.

VIII. PHOTOCHEMICAL STABILITY OF MOLECULAR SYSTEMS

In this Section we shall show in relation to specific examples how the photochemical stability of molecules can be related to their structures using the above theoretical results. In conformity with the initial task, we shall consider only the photochemical R–H bond dissociation reactions. Before proceeding to the consideration of specific systems, we shall define yet again the region of applicability of the concepts described. The most important hypothesis among these is that the change in the potential surface of the molecule in the excited state is little different from that in the ground state. Molecules with a small number of atoms (of the type of H_2O), in which there is a significant change in the geometrical characteristics of the system on electronic excitation due to the small number of bonds, constitute an evident exception. Molecules containing either a weak R–H bond, the excited orbitals of which have the minimum energy, constitute a less evident exception. The lowest excited state of such a system corresponds to local excitation of this bond, with a significant change in the nature of the dependence of the potential curve on the bond length. A characteristic example of this is provided by molecules containing an S–H bond (mercaptans). This can be readily demonstrated by comparing the absorption spectra of mercaptans and aliphatic sulphides. The absorption spectra of mercaptans are located further towards long wavelengths than the spectra of the sulphides[62]. The opposite relation is observed in oxygen- and nitrogen-substituted aliphatic compounds when O–H (N–H) bonds are replaced by O–C (N–C) bonds[1]. Aliphatic compounds containing C–C, C–H, C–N, C–O, C–S, N–H, and O–H (but not S–H) bonds are therefore the objects of our consideration.

In modern photochemistry, there are two situations differing in the methods whereby excited states are generated. For low intensities of the exciting light, the system in an excited state has not had sufficient time to absorb a second quantum. The evolution of the electronic states of the system in this situation is described by a simple kinetic scheme, where there is a possibility of transitions to the lowest electronic states only (at low temperatures). For high light intensities, the system, which is in the triplet state, can absorb a second light quantum with a high probability, this being accompanied by a transition to highly excited triplet states§. The photochemistry of molecules is in this case referred to as two-quantum photochemistry[23] and differs from the classical one-quantum photochemistry. As can be seen from the foregoing factors, in a theoretical treatment these two cases must also be distinguished. We shall examine the one-quantum case first.

1. Aromatic Hydrocarbons

The energy of the C–H bond in the molecules of aromatic hydrocarbons is 4.5 eV.[63] The rate of elimination of atoms from such systems cannot therefore exceed $10^2\ s^{-1}$ if the decomposition takes place from the ground vibrational state. The lifetime of the lowest singlet state of the benzene molecule, the energy of which is sufficient for the dissociation of the C–H bond, amounts to 10^{-7} s.[24] It follows from this that the quantum yield of the elimination of hydrogen atoms on excitation by the light corresponding to the first absorption band cannot exceed 10^{-5}. This value agrees with numerous experimental data[1].

When the benzene molecule is excited to high singlet states ($\lambda < 1849$ Å), the quantum yield of the cleavage of the C–H bond in the gas phase increases[65], which can be explained by several causes: (1) singlet–triplet conversion may lead to highly excited triplet states, where decomposition via a predissociative mechanism takes place. (2) Internal conversion can result in the formation of a highly vibrationally excited benzene molecule in the first singlet state, where the probability of the dissociation of a C–H bond may become very appreciable, in conformity with Eqn. (12). (3) Non-adiabatic decomposition with formation of a C_6H_5 radical in an electronically excited state may also make a definite contribution. All these mechanisms are unlikely in the condensed phase, where the rates of internal conversion and vibrational relaxation are high.

The introduction of alkyl substituents into the benzene molecule diminishes somewhat the photochemical stability of the molecule under the same excitation conditions. This was to be expected in view of the results described in Section V, because these molecules contain a C–H bond in the alkyl substituent with a dissociation energy of approximately 3.6 eV. Despite the fact that the bond is remote from π-electron system of the molecule, where the excitation is localised, calculations (see Section VI) have shown that the rate of its dissociation exceeds by

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§ For still higher excitation intensities, transitions from the lowest excited S_1 state to the upper singlet states also become significant[64], but transitions of this kind do not introduce any significantly new features into the photochemical behaviour of molecules, because this situation corresponds to low intensities of the high-frequency excitation field.

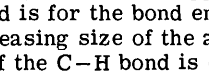
more than an order of magnitude the rate of dissociation of the bonds in the benzene ring. The quantum yield of the dissociation of the C–H bonds in the alkyl substituents of benzene (toluene, ethylbenzene, t-butylbenzene, mesitylene, and others[1]) exceeds 10^{-4}, which is greater by an order of magnitude than the corresponding value for benzene and agrees well with the estimated value of k quoted here.

Aromatic compounds (naphthalene, anthracene, etc.) having a more extensive chain of conjugated bonds than benzene and their substituted derivatives are still more stable. This is associated with the fact that the energy of the lowest singlet (and even more so triplet) states is insufficient for the dissociation of the C–H bonds.

2. Aliphatic Hydrocarbons

The dissociation energy of the C–H bonds in aliphatic hydrocarbons is approximately 4 eV.[63] Decomposition via a non-adiabatic mechanism cannot therefore contribute much to the formation of atomic hydrogen in the photolysis of paraffins, the quantum yield of which is approximately 0.1.[1,12,13] Decomposition via a predissociation mechanism in the singlet state arising on photoexcitation is forbidden, as shown in Section VI. The only real mechanism of the decomposition of paraffin molecules with elimination of a hydrogen atom therefore involves predissociative decomposition in the triplet states, whose energy (~6–7 eV) [44,46] is more than sufficient for this reaction. According to Plotnikov's estimates[44], the rate of the singlet–triplet conversion in paraffins should be high (~10^9–10^{10} s^{-1}). Quantities of the same order of magnitude may be obtained also for the rate of elimination of a hydrogen atom in triplet states. The molecular elimination of H_2 [67] and certain other processes compete with the singlet–triplet conversion. Only the fraction of the molecules which pass to the triplet states undergo decomposition with elimination of a hydrogen atom. This in fact explains the finding that, despite the high rate of elimination of a hydrogen atom, the quantum yield of this process is appreciably less than unity on photoexcitation of paraffin molecules. The atom produced should possess a considerable kinetic energy ($\geqslant$1 eV).

The set of experimental and theoretical results makes it possible to postulate a mechanism for the photochemical decomposition of paraffin in the lowest excited states with formation of hydrogen:



3. Aldehydes and Ketones

The lowest singlet state of aliphatic aldehydes and ketones is the $n\pi^*$ state, the energy of which is ~3.4–3.7 eV.[1,24] The experimental dissociation energies of the H–COR bond in aldehydes show an appreciable scatter, but the overall trend is for the bond energy to increase somewhat with increasing size of the alkyl group R. Thus the lowest energy of the C–H bond is estimated as 3.02 eV in formaldehyde and 3.69 eV in the CH_3CHO molecule[68]. If this is so, the dissociation of the C–H bond in formaldehyde via a non-adiabatic mechanism should be much faster than in the molecules of more complex aldehydes. Experimental data[1] confirm this conclusion: the elimination of atomic hydrogen is significant only in the photochemistry of formaldehyde and is not observed for more complex aldehydes.

The C–H bond dissociation energy in ketones is approximately 4 eV,[63] so that it exceeds the energy of the lowest excited singlet state. This explains the experimental finding that the elimination of a hydrogen atom on excitation of ketones with light corresponding to the first absorption band is not observed. Only for very high excitation energies (~6–7 eV), where predissociative decomposition via triplet states becomes possible, is there an appreciable contribution by reactions involving the elimination of a hydrogen atom (acetone in the gas phase)[1].

4. Substituted Aliphatic Compounds

The energy of the lowest singlet excited state of aliphatic alcohols, ethers, and amines is of the $n\sigma^*$ type and amounts to ~6 eV,[1,69] while the C–H bond dissociation energy in these compounds is ~4 eV.[63] It is seen from these data that, although the dissociation of C–H bonds via a non-adiabatic mechanism in $S_{n\sigma^*}$ states is possible, its contribution is small. The predissociative decomposition in triplet states, which are located in the vicinity of the lowest singlet, is much more effective. Since the elimination of an H_2 molecule competes with the intercombination conversion process which precedes the decomposition, as in aliphatic hydrocarbons, the elimination of a hydrogen atom is not the only (and perhaps not the decisive) reaction. The introduction into the molecule of O, N, S, etc. atoms with a nuclear charge greater than that of a carbon atoms leads to an increase of the rate of the singlet–triplet conversion[44], which should result in an increased role of the hydrogen atom elimination reaction of such molecules, compared with hydrocarbon molecules. Here one must of course take into account the change in the position of the lowest triplet state on substitution. It may turn out that substitution leads to a sharp decrease of the energy of the T state, which increases the stability of the molecule. (This in fact occurs when an S atom is introduced into the molecule of an aliphatic sulphide.) The experimental data available hitherto[1] confirm this tendency, since the yield of atomic hydrogen in the photolysis of alcohols, ethers, and amines is always higher than in the photolysis of paraffins. Unfortunately the mechanism of the photolysis of aliphatic compounds with substituents has been studied less thoroughly than that of aliphatic hydrocarbons. This factor precludes a quantitative comparison of the theoretical and experimental results.

Aromatic alcohols, ethers, and amines are much more stable than their aliphatic analogues, which can be accounted for by the low energy of the triplet states of aromatic compounds

5. Certain Radicals

The bond energy D of the hydrogen atom in many radicals is greatly reduced compared with its value in the initial molecules[63]:

R	H—CO	C_2H_5	C_2H_3	H—CHOH
D, eV	~0.8	~1.7	~1.7	~1.2

Comparison of the above data with the results in Section V shows that radicals are as a rule less stable than the parent molecules. Indeed, for a bond energy $\lesssim 2$ eV, the rate of elimination of the hydrogen atom exceeds 10^9 s^{-1}, i.e. is higher than the rate of radiative transitions. For bond energies less than ~1 eV, the decomposition takes place with a quantum yield of ~1, if the excitation energy exceeds the energy threshold of the reaction, regardless of the position of the lowest excited state. The available experimental data for photochemical reactions of radicals [22] confirm this conclusion.

6. Radical-cations Derived from Organic Molecules

The R–H bond energy in radical-cations derived from organic molecules depends very markedly on their structure. Its value (D^+) may be expressed in terms of the energy of the R–H bond in the initial molecule (D) and the difference between the ionisation potentials (ΔI) of the molecule and the radical: $D^+ = D - \Delta I$. In most cases $\Delta I > 0$ and $D^+ < D$. Hence it follows that radical-cations are as a rule less stable than the initial molecules. (There are also exceptions. Thus $\Delta I < 0$ for the aniline molecule.)

ΔI for aliphatic compounds is 2–3 eV,[63] but in the case of aromatic compounds it is appreciably less. Thus it amounts to ~1.4 eV for the toluene molecule[63]. These data show that the energy of the C–H(R–H) bond in radical-cations derived from aliphatic molecules is 1–2 eV, while the value for radical-cations obtained from aromatic molecules is much higher, being close to ~3 eV. We may note that the C–H bond energy in the CH_2 groups of the radical-cations derived from aliphatic hydrocarbons is smaller by 0.5 eV than the corresponding value for the CH_3 groups.

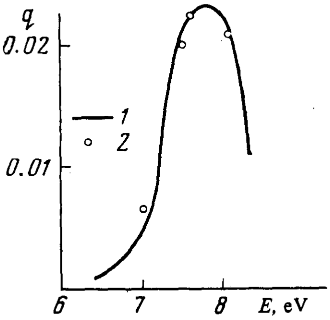


Figure 7. Dependence of the quantum yield of the elimination of a hydrogen atom from the triphenylmethane molecule on the triplet excitation energy: 1) theory; 2) experiment[61].

Comparison of the above data with the results of Section V shows that the radical-cations of aliphatic compounds are much less stable than those of aromatic compounds. This conclusion has been confirmed experimentally [70,71]. The fact that the energy of the first excited doublet state of the radical-cations is frequently small (~1–2 eV) [26,59,60] provides further justification for the above conclusion. Whereas the rate constant for the elimination of a hydrogen atom from aliphatic compounds is high and the elimination process may compete with internal conversion, in aromatic compounds it is almost completely suppressed. The hydrogen atom should be eliminated with a high probability from the central part of the radical-cations derived from paraffins.

We shall now consider briefly the two-quantum excitation of organic molecules. Such excitation gives rise to highly excited triplet states, where C–H bonds may be dissociated via a predissociative mechanism[72]. (This process is not of course the only one possible. Highly excited triplet states very frequently undergo ionisation or preionisation, and not predissociation, particularly when polar solvents are used[23,73].) The case of the two-quantum excitation of molecules is of particular interest, since it makes it possible to compare the theoretical result for the dependence of the probability of predissociation on the energy of the excited state (see Section VI) with experiment.

The $k(E)$ relation has been studied experimentally[61]. Fig. 7 illustrates the theoretical relation, calculated by Eqn.(25) using the parameters characteristic of the C–H bond, together with the experimental results. Evidently there is not only qualitative, but also quantitative agreement between the theoretical and experimental data.

The above examples show how the causes of the different photochemical stabilities of molecular systems having different structures may be understood using theoretical conclusions.

IX. RADIATION-CHEMICAL STABILITY OF MOLECULAR SYSTEMS

The yield of stabilised radicals is used as a quantitative criterion of the stability of molecules in the radiation chemistry of condensed media at low temperatures, because hydrogen atoms are not detected in most cases. The possibility of employing these data to compare the theoretical conclusions of Sections V and VI with experiment is not evident. Strictly speaking, the theory described is applicable to the yield of atomic hydrogen and its use to describe the yield of radicals may be to some extent qualitative. The point is that unimolecular reactions are not the only possible pathway to the formation of radicals. Radicals whose structure is identical with that of the radicals obtained from the parent molecules following the elimination of a hydrogen atom may arise as a result of the ion–molecule reaction

$$RH^+ + RH = R^{\cdot} + RH_2^+$$

and others. The relative contributions of unimolecular and other radical-generating processes are not at present known with sufficient accuracy[21], but the yield of radicals is usually appreciably (by a factor greater than 2) higher than that of stabilised electrons and therefore radical-cations[19]. Hence follows the conclusion that the unimolecular pathway to the formation of radicals is one of the most important. Apart from the causes already indicated, yet another factor prevents a quantitative comparison of theoretical conclusions with experiment: the amount of radicals detected may not agree with its initial value, because the initial radicals may disappear in numerous reactions (disproportionation, recombination, isomerisation, etc.). For this and other reasons (see below), in comparing the conclusions of Sections V and VI with experiment one must employ data obtained at temperatures as low as possible.

In describing unimolecular hydrogen elimination process in radiation chemistry, one must bear in mind the following two factors. The effect of ionising radiation on molecular media leads to the formation of not only neutral excited molecules, but also of electronically excited radical-cations. According to estimates[74], the yields of ionised and electronically excited species are approximately the same. The decomposition of radical-cations with elimination of a hydrogen atom and subsequent recombination of the radical-cation R^+ with an electron constitutes an additional pathway (unimolecular in the sense of the formation of hydrogen atoms) to the formation of radicals in radiolysis, compared with photolysis. The natures of the primary excited states of molecules formed on radiolysis and on excitation by light are different. Under the conditions of radiolysis, excitation takes place when electrons collide with the molecules. The optically forbidden singlet—triplet transitions become allowed under these conditions (particularly for the resonance energies of the electrons) and the possibility of the excitation of triplet states, bypassing singlet states, arises.

There is yet another possibility of the direct excitation of triplet states, associated with the recombination reactions of radical-cations and electrons. The ratio of the amount of triplet states formed under these conditions to the amount of singlet states is three, provided that the orientations of the spins of the unpaired electron of the radical-cation and the electron with which it recombines are independent[75]. Under real conditions, this ratio depends also on a number of factors [the spin relaxation time and the distribution of radical-cations and electrons (see, for example, the paper of Magee and Huang[76] and the literature quoted therein¶)].

The direct formation of excited triplet molecules on radiolysis should lead to an increase of the yield of atomic hydrogen compared with its yield on photolysis. Experimental data confirm this conclusion. Thus the ratio of the yield of atomic hydrogen to that of molecular hydrogen is close to unity in the radiolysis of aliphatic hydrocarbons[3]. In photolysis the ratio is approximately 0.1 (see Section VIII).

We shall now consider specific systems. In order to demonstrate the generality of the approach, we shall divide molecules into groups in terms of their radiation-chemical stabilities and not chemical classes. All organic compounds can be divided arbitrarily into three groups: compounds in which the yield of radicals per 100 eV of absorbed energy $G > 1$, compounds for which $G \simeq 1$, and compounds for which $G \ll 1$. The reasons for this subdivision will be made clear below.

1. The first group of compounds includes aliphatic hydrocarbons, alcohols, ethers, amines, and many polymers. Table 1 lists the experimental values of G for these compounds and includes the energies of the lowest triplet state (E_T) and the C–H bond dissociation energies in a neutral molecule (L).[63] The value of E_T for the majority of molecules was determined as the difference between the energy of the lowest singlet state[1,68] and the singlet–triplet splitting. The latter was assumed to be 1 eV for aliphatic hydrocarbons ($\sigma\sigma^*$ states) and 0.5 eV for the remaining compounds ($n\sigma^*$ states)[44]. The values of E_T thus obtained are apparently somewhat higher than the true values[66], but for our purposes an improvement in the accuracy of E_T is unimportant. We may also note that all these compounds, with the exception of amines, have a high ionisation potential ($\geqslant$9 eV). Depending on the molecular structure, its value for amines varies from 7.6 eV to 9 eV.[63] The data in Table 1 permit the conclusion that there is a high probability of the elimination of hydrogen atoms via a predissociative mechanism from molecules of compounds in the first group in the excited triplet state.

Table 1. The values of G, E_T, and D for compounds of the first group.

Compound	G	References	E_T, eV	D, eV
Cyclohexane	4	77	7	4,08
n-Hexane	4.7	20	7	4,1
n-Heptane	4.4	20	7	4,1
n-Decane	3.6	20	7	4.1
Methyl alcohol	5.2	78	6,4	3.96
Ethyl alcohol	6.4	78	6,4	3.9
Aliphatic amines	3—5	79	5.1	4.05
Ethers	2—4	79	6	3.9
Polyethylene	5.8	8	7	4
Polypropylene	4.8	8	7	3.9
Poly(vinyl alcohol)	2.8	8	6	3.9
Polyvinylformal	5	8	6,4	3.9
Polyamides	2,4—3.1	8	5.3	3.9
Poly(ethylene glucol)	4—4.8	8	6	3.9

Since the ionisation potentials of the compounds listed in Table 1 are high, one may expect the formation of a large number of highly excited triplet states on charge recombination. The hydrogen atom formed in this reaction has a high kinetic energy and in its first collision may abstract a hydrogen atom from a neighbouring molecule. This may explain the stereospecificity of the formation of radical pairs in solid paraffins[80]. The energy of the C–H(O–H, N–H) bonds in the radical-cations derived from the molecules of the first group is ~1 eV.[21,71] In conformity with the results in Section V, this leads to high rate constants for the elimination of a hydrogen atom from electronically excited radical-cations.

Thus both pathways to the formation of radicals discussed here occur with a high probability for compounds of the first group. It is so far difficult to estimate their relative contributions.

2. The second group includes compounds with $G \simeq 1$. Table 2 presents examples of some of them. The data listed in this table show that the energy E_T is in most cases (where it is known exactly) lower than the energy of the C–H bond. In conformity with the results in section VI, the probability of the elimination of a hydrogen atom from the excited molecules is determined by the ratio of the rate constants for the elimination and internal conversion processes. It is readily seen that the latter depends in this instance on the molecular structure. In

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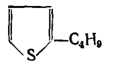
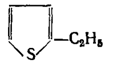
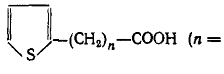
¶ Apart from the factors quoted by Magee and Huang[76], the ratio of the yields of triplets and singlets is also influenced by processes involving the polarisation of the medium, the electronic matrix element of the transition, and the Franck–Condon factor of the vibrations of the molecules and the medium. These problems have not as yet been investigated theoretically.

highly excited reactive $\sigma\sigma^*$ and $\pi\sigma^*$ ($\sigma\pi^*$) states the excitation is delocalised over the entire molecule. The lowest triplet state is localised in a comparatively small part of the molecule (at a benzene ring, a double bond, or an S–S bond). The spatial separation of the excited states causes a decrease of the rate of internal conversion between highly excited states and the $\pi\pi^*$ ($n\sigma^*$) state with increase of the number of CH_2 group (N) as N^{-1}. When $N \gg 1$, conversion processes cannot suppress the decomposition processes. All the foregoing considerations apply also to the excited states of the radical-cations derived from the molecules of the second group.

Table 2. The values of G, E_T, and D for compounds of the second group.

Compound	G	References	E_T, eV	D, eV
Ph—$C_{17}H_{35}$	0.8	81	3.5	3.7
Ph—C_9H_{19}	0.59	81	3.5	3.7
Ph—C_7H_{15}	0.46	81	3.5	3.7
Ph—C_5H_{11}	0.55	82	3.5	3.7
Ph—C_4H_9	0.24	81	3.5	3.7
Ph—C_2H_5	0.19	81	3.5	3.7
	0.8	79	<4	~4
	0.2	79	<4	~4
$C_{14}H_{29}$—S—S—$C_{14}H_{29}$	1.1	79	<4	~4
$C_{12}H_{25}$—S—S—$C_{12}H_{25}$	1	79	<4	~4
C_8H_{17}—S—S—C_8H_{17}	0.35	79	<4	~4
C_4H_9—S—S—C_4H_9	0.2	79	<4	~4
 ($n = 4$—12)	1	79	<4	~4

The second group thus includes compounds where one or both of the given pathways to the formation of radicals are incompletely suppressed. Some of the compounds of the second group should be included in the third group. We placed them in Table 2 in order to demonstrate the continuity of the transition from the second to the third group.

The term intramolecular energy transfer is used in radiation chemistry instead of the term internal conversion. In other respects the above ideas are the same as those developed in studies by Voevodskii and coworkers[2].

3. The third group includes compounds with the highest radiation-chemical stability (Table 3). The data in Table 3 show that the energy of the lowest triplet state[24,27] of these compounds is lower than the C–H bond dissociation energy. One should not expect for these compounds anomalously long internal conversion times in the highest triplet states, since the excited states of these compounds are not spatially separated. The elimination of a hydrogen atom from the molecules in the highest triplet states is suppressed by internal conversion. An increase of the number of π electrons leads to a decrease of the rate constant for the elimination of a hydrogen atom (see Section VI) and to an increase of the internal conversion rate constant owing to the increase of the density of electronic states. This explains the decrease of G with the increase of the number of conjugated bonds in the molecule.

The energy of the bonds involving the hydrogen atoms in the radical-cations derived from the majority of the compounds listed in Table 3 is high (~3 eV [63,71]), so that the non-adiabatic reaction involving the elimination of a hydrogen atom from a radical-cation cannot compete with the decomposition reactions in the excited states. The ionisation potentials of all the compounds in the third group do not exceed 9 eV [63] and decrease sharply on passing to the condensed phase[57,58]. This means that the probability of the formation of highly excited triplet states on charge recombination is low and that their lifetime is short owing to ionisation processes. With increase of the polarity of the medium, the probability of the formation and the lifetime of the highest triplet states diminish, which may explain the decrease of G with increasing polarity of the medium (cf. for example, benzene and benzoic acid).

Table 3. The values of G, E_T, and D for compounds of the third group.

Compound	G	Refs.	E_T, eV	D, eV
Toluene	0.3	2	3.55	3.7
Benzene	0.2	2	3.66	4.7
Phenylacetylene	0.08	83	3.1	4.7
Diphenylacetylene	0.04	83	3.1	4.7
Biphenyl	0.05	82	2.8	4.7
Diphenyl disulphide	0.06	79	3.5	4.7
Thiophen	0.18	79	<4	4.7
Benzoic acid	0.05	2	3.35	4.7
Polystyrene	0.2	8	3.5	3.7
Poly(ethylene terephthalate)	0.4	8	3.5	3.7

The above results demonstrate the usefulness of the attempt to explain the low-temperature radiation-chemical stability of molecules (in the narrow sense under consideration) taking into account only the unimolecular radical formation reactions. The absence of contradictions between the theoretical and experimental data permits certain hypotheses concerning the possible role of the remaining radical formation processes, in the first place the role of ion–molecule reactions: the role of these processes at low temperatures is either small or the probability of their occurrence is correlated with the probability of unimolecular reactions. The discussion of this problem is outside the scope of the initial aim of this review and we shall therefore confine ourselves to certain general remarks.

The widely held view in radiation chemistry that ion–molecule reactions in the condensed phase make an appreciable (decisive according to some workers[19]) contribution to the formation of radicals in low-temperature radiolysis is based on the high cross-sections of these reactions in the gase phase[71,84,85]. However, it is incorrect to assume that these results are also valid for the condensed phase.

It follows from the general theory of reactions involving a change in charge distribution in the condensed phase[86-88] that their rates depend on the energy of the reorganisation (repolarisation) of the medium, decreasing exponentially with its increase. This leads to a non-zero activation energy for ion–molecule reactions in the condensed phase. The presence of an activation energy has been noted for ion–molecule reactions even of weakly polarised compounds such as molecular hydrogen[89]. At low temperatures ($k_BT \ll E_a$, where E_a is the activation energy) ion–molecule reactions therefore make a small contribution to the formation of radicals (naturally provided that $E_a \neq 0$).

The values of E_a are at present unknown, so that it is difficult to specify the temperature below which ion–molecule reactions are unimportant for the given system. Experimental studies of the temperature dependence of the yield of radicals at $T < 77$ K may be of primary importance in this connection. Since the rates of unimolecular reactions involving the elimination of atomic hydrogen are independent of temperature, such data make it possible to estimate the contributions of different pathways to the formation of radicals at low temperatures. (We may note that the yield of CH_3 radicals in the radiolysis of methane at 4.2 K is the same as the yield of atomic hydrogen[90].)

Another important difference between the condensed and gas phases, which must be taken into account in considering ion–molecule reactions, is that the lifetime of the separated charges in non-polar media is extremely short ($\lesssim 10^{-10}$ s).[3,91] The recombination process will thus compete with ion–molecule reactions, increasing the contribution of the unimolecular radical formation process.

Unfortunately there is as yet no common point of view on the problem of the relation between ion–molecule reactions and the electronic structures of the species involved in them. One can only claim that aliphatic molecules and cations show a greater tendency to undergo such reactions than aromatic species, because the ionisation of aromatic molecules does not involve R–H (C–H) bonds. The probability of ion–molecule reactions is particularly high for aliphatic alcohols and amines, because the ionisation of their molecules involves the elimination of an n electron, together with an oxygen or nitrogen atom, and a significant decrease of the proton elimination energy.

Thus it is to be expected that the probability of ion–molecule radical-formation reactions is correlated with the probability of unimolecular reactions, and that the contribution of the latter at low temperatures is decisive, although exceptions are possible.

The contents of this section are part of the general theory of the radiation-chemical behaviour of molecules The creation of this theory is a task for the future.

X. CONCLUSION

The results quoted demonstrate the usefulness of the application of theoretical considerations in the interpretation of the photochemical and radiation-chemical properties of molecular systems. There is no doubt that interesting results are to be expected along these lines in the future. We believe that the theory will develop along two paths: the refinement of the models already examined and the development of models of processes which have not as yet been investigated. In refining the models, one should bear in mind primarily the possibility of reactions involving the elimination of a hydrogen atom and the formation of radicals in electronically excited states. This path is of considerable importance in the vacuum photolysis of gas-phase molecules. Among problems which have not been investigated as yet, the development of the theory of the non-adiabatic and predissociative elimination of molecular hydrogen, of the dissociative addition of electrons, and of the formation of excited states by recombination is important. The problem of the theoretical description of ion–molecule reactions in the condensed phase is of particular interest. The successful solution of such problems requires further experimental investigation of the spectra of radicals and radical-cations and of the temperature dependence of the yield of radicals in radiolysis.

XI. APPENDIX

Here we shall describe the estimation of the electronic component of the matrix element of the non-adiabatic operator. The expression for β can be transformed into

$$\beta = \left\langle i \left| \frac{\partial U}{\partial x} \right| f \right\rangle_{x=0} [\Delta E_{fi}(0)]^{-1}, \tag{A.1}$$

where U is the operator of the Coulombic interaction of the electrons and nuclei of the system and $\Delta E_{fi}(0)$ is the difference between the electronic energy levels f and i at the point corresponding to the equilibrium configuration. By choosing the system in such a way that the x axis coincides with the direction of the R–H bond, one can obtain for the derivative $\partial U/\partial x$

$$\frac{\partial U}{\partial x} = \sum_i \left[\frac{z_1 e^2 m_2 (X_1 - x_i)}{(m_1 + m_2)\,|\mathbf{R}_1 - \mathbf{r}_i|^3} - \frac{z_2 e^2 m_1 (X_2 - x_i)}{(m_1 + m_2)\,|\mathbf{R}_1 - \mathbf{r}_i|^3} \right], \tag{A.2}$$

where m_1 and m_2 are the masses, z_1 and z_2 the effective charges, $\mathbf{R}_1$ and $\mathbf{R}_2$ the radius-vectors, X_1 and X_2 their x components for the nuclei of the hydrogen atom and the atom to which it is linked, and $\mathbf{r}_i$ and x_i are the radius vector and its x component for the ith electron. The operator (A.2) is of the one-electron type and the general expression for its matrix elements between arbitrary configurations can be found in Kaplan's book[92]. If $|i\rangle$ is the excited state and $|f\rangle$ is the ground state, then

$$\left\langle i \left| \frac{\partial U}{\partial x} \right| f \right\rangle = \sqrt{2} \left\langle \varphi_i \left| \frac{\partial U}{\partial x} \right| \varphi_f \right\rangle, \tag{A.3}$$

where φ_i and φ_f are the molecular orbitals between which the electronic transition takes place. In other cases the expression for the numerator in Eqn. (A.1) differs from that in Eqn. (A.3) by an unimportant numerical multiplier. When φ_i and φ_f are described by a linear combination of atomic orbitals. The main contribution to β comes in most cases from two-centre integrals for the interaction of the electrons of the atom to which the hydrogen atom is linked with the nucleus of the hydrogen atom. Their calculation presents no difficulty, since they are expressed in terms of the derivatives of two-centre quantum-chemical integrals with respect to the internuclear distance R.[93] For example, in the case of $\pi-\pi^*$ transitions of aromatic molecules, this integral is

$$\gamma = \left[2p_z 2p_z \left| \frac{X_1 - x}{|\mathbf{R}' - \mathbf{r}|^3} \right.\right] = \frac{1}{R^2} - \frac{18}{\alpha^2 R^4} + \left(\frac{18}{\alpha^2 R^4} + \frac{18}{\alpha R^3} + \frac{8}{R^2} + \frac{2\alpha}{R} + \frac{\alpha^2}{4} \right) e^{-\alpha R}, \tag{A.4}$$

where α is the Slater charge of the carbon atom for the $2p_z$ functions. Assuming that $R = 2$ a.u., and $\alpha = 3$, we obtain $\gamma \simeq 0.15$ a.u. The integrals with other functions of the valence shell of the carbon atom and other atoms in the Second Period have similar values. The expression $\gamma = R^{-2}$ can be used for estimates, provided that $R > 3$ a.u.

Taking into account only two-centre integrals for the interaction of atoms with the nearest carbon atom, we obtain the following expression for β in the decomposition of aromatic hydrocarbons in the $\pi\pi^*$ states:

$$\beta = C_{ni} C_{nf} \gamma (\Delta E_{if}(0))^{-1},$$

where C_{ni} and C_{nf} are the coefficients of the expansion of φ_i and φ_f with respect to the atomic orbitals of the carbon atom from which the hydrogen atom is eliminated. If the molecule contains N carbon atoms, then $C_{ni} \simeq C_{nf} \simeq N^{1/2}$ and $\beta \simeq N^{-1}\gamma[\Delta E_{if}(0)]^{-1}$. After summation with respect to all the hydrogen atoms, we find that $k \simeq N^{-1}$. Thus the stability of molecules increases with increase in the number of conjugated bonds. The values $N \lesssim 6$ are of real interest. Bearing in mind that $\Delta E_{if} \simeq 0.1$ a.u., we obtain $|\beta|^2 \simeq 2$ a.u. For molecules containing a large number of bonds, $|\beta|^2$ is much smaller than this value.

In the decomposition of molecules in $\sigma\sigma^*$ states, which can be described in terms of the strong bond approximation, k is independent of N, and the same value (i.e. 2 a.u.) may be used for $|\beta|^2$. If the decomposition takes place in the $n\pi^*$ and $n\sigma^*$ states of molecules or $\sigma\sigma^*$ states of radical-cations, then k is independent of molecular size owing to the localisation of states, and it may be assumed that $|\beta|^2 \simeq 2$ a.u.

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^{13}C NMR Spectroscopy of Substituted Cyclohexanes

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New possibilities are demonstrated in the study of the conformations and dynamics of ring inversion in substituted cyclohexanes by ^{13}C NMR spectroscopy compared with other methods of chemical and physical analysis.
The bibliography includes 106 references

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I. INTRODUCTION

^{13}C NMR spectroscopy employing the natural abundance of the ^{13}C isotope ($\sim$1.1%) has become extremely common in recent years. Progress in the technique of the recording of weak NMR signals, due to the introduction of pulsed Fourier transform NMR spectroscopy (FT),[1] permitted a wide-scale employment of this method in studies on complex objects, particularly natural products. The general principles of ^{13}C NMR and its applications are described in a number of reviews[2,3] and monographs[4-6]. Among the applications of the method, special mention should be made of stereochemical research associated with the determination of the steric structures of organic molecules. The term "stereochemical research" is used in its widest sense, including the study of the possible conformations (conformational analysis) and the kinetics of intramolecular rearrangements (dynamic stereochemistry).

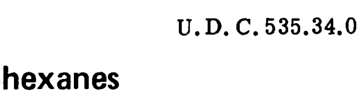
The aim of the present review is to analyse the results of the application of the ^{13}C NMR method to the study of substituted cyclohexanes. These compounds are of practical interest for organic chemistry and are traditional objects of classical conformational analysis[7].

II. CONFORMATIONAL ANALYSIS AND DYNAMIC STEREOCHEMISTRY OF SUBSTITUTED CYCLOHEXANES

Studies on the structures of cyclohexane derivatives have an extremely long history, the main landmarks of which are the classical studies by Sachse[8], Hassel[9], and Barton[10]. Starting from the 1950s, these compounds have been vigorously investigated with the aid of various chemical and physical methods; the numerous publications on this topic are analysed in a number of monographs[11,12] and reviews[13-15].

The present review deals only with the problems of experimental conformational analysis. Dashevskii's monograph[12] gives some idea about the tasks of theoretical conformational analysis, associated with calculations of the energies and geometrical structures of the conformers.

The aims of conformational analysis and the fundamental terminology employed in reports on the structures of substituted cyclohexanes can be illustrated in relation to monosubstituted derivatives $C_6H_{11}X$. One usually considers the equilibrium between only two forms (conformers), with the axial and equatorial orientations of the substituent X respectively:



(Ia) (Ie)

The conformational equilibrium is regarded as involving a rapid interconversion or inversion of the ring, $(Ia) \rightleftharpoons (Ie)$, which can be described by two rate constants:

$$k_{ae} = \varkappa \frac{kT}{h} \exp(-\Delta G^{\neq}_{ae}/RT),$$
$$k_{ea} = \varkappa \frac{kT}{h} \exp(-\Delta G^{\neq}_{ea}/RT), \quad (1)$$

where κ is the transmission coefficient and $\Delta G^{\neq}$ the free energy of activation;

$$\Delta G^{\neq} = \Delta H^{\neq} - T\Delta S^{\neq}, \quad (2)$$

where $\Delta H^{\neq}$ and $\Delta S^{\neq}$ are the enthalpy and entropy of activation. In the general case $k_{ae} \neq k_{ea}$ (a non-degenerate process). The equilibrium in the reaction $(Ia) \rightleftharpoons (Ie)$ may be characterised by the equilibrium constant K:

$$K = p_e/p_a = k_{ae}/k_{ea} = \exp(-\Delta G^0/RT), \quad (3)$$

where p_a and p_e are the equilibrium concentrations of the axial and equatorial conformers, it being assumed that

$$p_a + p_e = 1. \quad (4)$$

The quantity $-\Delta G°$ is called the conformational energy; the term "A-value" is frequently used:

$$A = -\Delta G^0 = G_a - G_e, \quad (5)$$

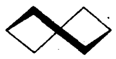
where G_a and G_e are the free energies of the axial and equatorial conformers.

In the general case, when several substituents are present, the conformational equilibrium also involves only two conformers (A_1 and A_2); the equilibrium constant and the conformational energy for the process $(A_1) \rightleftharpoons (A_2)$ are defined as follows: $K = p_2/p_1$ and $-\Delta G° = G_1 - G_2$. In the specific instance of monosubstituted cyclohexanes it is assumed that $A_1 = (Ia)$ and $A_2 = (Ie)$.

Conformational Analysis

The main task in conformational analysis is the experimental determination of the equilibrium concentrations of the conformers. Evidently this task includes as a necessary stage the proof that only two forms are involved in the equilibrium at appreciable concentrations. Together with the *a*- and *e*-conformers examined above, which are derived from the chair conformation, other conformers derived from the boat (II) or twist-boat (III) conformations are also sometimes considered:


(II)


(III)

Numerous theoretical estimates of the energies of a wide variety of non-chair forms of cyclohexane[16,17] have shown that the hypothesis that the chair form is most favourable is in fact justified, but the experimental proof of this was obtained only quite recently by Anet and coworkers[18]. These investigators detected the non-chair forms of cyclohexane by the method involving rapid freezing of the high-temperature equilibrium. For this purpose, gaseous cyclohexane, heated to approximately 800 K, was condensed, after vacuum evaporation, onto a CsI plate cooled to 20 K. It was thus possible to assume that the composition of the conformers in the condensate reflects the nature of the conformational equilibrium at high temperatures. It was shown by infrared spectroscopy that, together with the chair form, the condensate contains the twist-boat form. Estimates showed that the enthalpy of the twist-boat conformation exceeds by 5.5 kcal mole^{-1} that of the chair conformation. Assuming that the entropy contribution is close to zero, one may conclude that the content of the twist-form at room temperature does not exceed 0.01%. In the study of the conformational equilibria of substituted cyclohexanes, the negligible contribution of the non-chair forms is assumed without proof.

In order to determine the conformational equilibrium constant K, various methods have been used; Jensen and Bushweller[15] concluded on the basis of a comparison of numerous investigations that the method involving the measurement of the integrated intensities in high-temperature ^{1}H NMR spectra is the most accurate. On the basis of this method, the authors[15] proposed a system of "best" (i.e. most accurate) A-values for a number of substituents X. However, in view of the difficulty of the interpretation of the ^{1}H NMR spectra, the method cannot be regarded as a universal procedure for the measurement of the equilibrium constants K, which has been confirmed by the results of certain studies[13,15].

Investigators as a rule confine themselves to the determination of the conformational equilibrium constant at a single temperature, which permits the subsequent determination of the free energy ΔG_T at the same temperature. Naturally, on a wider scale conformational analysis involves the determination of the values of K over a fairly wide range of temperatures and the calculation from the $K(T)$ relation of the enthalpies and entropies of the reversible process (ΔH° and ΔS°).

An important feature of studies on conformational equilibria, consisting in the necessity to take into account the influence of intermolecular interactions (i.e. of the medium), should be noted. In many instances the influence of the medium is very significant[14,19]; this factor hinders the comparison of the results of different studies carried out in different media. As a rule equilibrium constants are measured by NMR in solutions where the test compound can be subjected to different chemical or physical influences. Thus there is a risk of the incorrect application of the parameters of the conformational equilibrium obtained in one solvent (for example in carbon disulphide, which is most suitable for NMR studies) to other conditions.

This factor, in particular, necessitates a certain amount of caution in comparing the results of studies on conformational equilibrium in almost neutral solutions and in solutions with added paramagnetic shift reagents[20], where additional complex-formation processes undoubtedly occur.

The Study of the Properties of Individual Conformers

This involves the investigation of the complete geometry of the conformers and also, in principle, the study of their other chemical and physical properties. This aspect is in fact of fundamental interest for theoretical organic chemistry in connection with the search for conformational features of molecules responsible for the selective courses of chemical reactions. Studies in this field constitute an important stage on the way to an effective employment of cyclohexane derivatives in fields such as pharmacology and the chemistry of insecticides and perfumes.

The Study of the Dynamics of the Conformational Transformation (Ring Inversion)

This involves the determination of the rate constants for ring inversion k_{ae} and k_{ea} and the calculation from these data of the free energies of activation $\Delta G^{\neq}_{ae}$ and $\Delta G^{\neq}_{ea}$. Within a wider framework, the study of the dynamics of ring inversion includes the determination of the rate constants over a wide temperature range and the calculation of the enthalpy ($\Delta H^{\neq}$) and entropy ($\Delta S^{\neq}$) of activation. The easiest method for the investigation of the dynamics of ring inversion in substituted cyclohexanes is NMR, which makes it possible to determine the rates of chemical processes from characteristic dynamic effects in the spectra[21-23].

The solution of the above problems requires the use of the entire set of the chemical and physical methods available at present. However, the specific limitations characteristic of particular methods sharply restrict the region of their applicability. Furthermore, there exist many limitations due to the specific features of the compound investigated, namely the chemical instability of the compound, its low solubility, and the narrow range of temperatures employed. Attention should also be drawn to certain limitations which are rarely mentioned in the literature but which are extremely fundamental. One of these is associated with the methodological difficulties in the isolation of the individual conformers, which requires the use of a special low-temperature technique. Only one report is at present available[24], concerning the isolation by low-temperature multistage recrystallisation of the equatorial conformer of chlorocylcohexane. Analysis of studies on polysubstituted cyclohexane has shown that even the much simpler problem of separating a mixture of isomers entails significant technical difficulties[45]. These difficulties apparently arise from the inadequate knowledge of the adsorption of substituted cyclohexanes. Another fundamental difficulty is caused by the lack of methods for the investigation of strongly displaced equilibria (in other words of high-energy conformations). The relative error of the methods of measurements used in conformational analysis as a rule increases sharply with increase of the equilibrium constant. A conformational energy ≥2 kcal mole^{-1} corresponds to equilibrium constants of 200 and above and the study of the conformational equilibrium becomes virtually impossible.

New possibilities arising from ^{13}C NMR spectroscopy in the solution of the problems formulated above are discussed below. Before describing them, we shall deal with the general characteristics of the method.

III. ^{13}C NMR SPECTROSCOPY. GENERAL CHARACTERISTICS, SCOPE, AND LIMITATIONS

The vast majority of measurements of ^{13}C NMR spectra are nowadays performed by pulsed Fourier NMR. As a rule the ^{13}C NMR spectra are recorded under the conditions of the complete suppression of spin–spin interaction with protons. In commercial NMR spectrometers the suppression of the interaction with protons (or proton decoupling) is achieved with the aid of the noise modulation of the high-frequency field, the carrier frequency of which is the same as the resonance frequency of protons. Proton decoupling is accompanied not only by the merging of the multiplets but also by an increase of the integrated signal intensities as a result of specific cross-relaxation phenomena arising on proton pumping (the so called Nuclear Overhauser Effect (NOE). Thus proton uncoupling leads to an evident simplification of the spectra; one line in the ^{13}C–{H} NMR spectrum corresponds to each chemically non-equivalent carbon atom in the molecule. The position of this line in the spectrum relative to the line of the reference substance, which is tetramethylsilane $(CH_3)_4Si$, or the chemical shift of the ^{13}C nucleus is the most important spectroscopic parameter. Numerous data quoted in monographs[4,5] have shown that ^{13}C nuclei are more effective "indicators" of chemical non-equivalence than, for example, protons. Comparison of the range of variation of the chemical shifts of ^{13}C and ^{1}H nuclei, $\Delta\delta(^{13}C)$ and $\Delta\delta(^{1}H)$, carried out in a number of studies[4,5,25] for the corresponding series of model compounds showed that

$$\Delta\delta\,(^{13}C) = k\Delta\delta\,(^{1}H), \qquad (6)$$

where the proportionality coefficient is 10–30 (depending on the series of compounds).

These two factors, namely the simple form of the ^{13}C–{H} NMR spectra and the high sensitivity of the chemical shift of ^{13}C nuclei to changes in the electronic environment were in fact responsible for the great interest by chemists in ^{13}C NMR.

In order to assess the nature and amount of information which can be obtained from ^{13}C NMR spectra, it is sufficient to examine the results of the study of the conformational state of chlorocyclohexane, a compound typical for the series under consideration[26]. The ^{13}C–{H} NMR spectra of chlorocylcohexane, measured in the temperature range from 193 to 273 K, are presented in Fig. 1. The changes observed in the spectra with increase of temperature indicate the occurrence of chemical exchange [in the present case of the conformational transformation (I*a*) ⇌ (I*e*)]. Two groups of signals (four signals in each group with the intensity ratios 1 : 2 : 2 : 1) can be distinguished in the spectrum measured at 193 K and referring to the conformers (I*e*) and (I*a*). The lower-intensity signals refer to the conformer (I*a*), since it had been shown previously for chlorocyclohexane[9] that $K = p_e/p_a > 1$. Further assignment of the signals to $C_\alpha(C_1)$, $C_\beta(C_2, C_6)$, $C_\gamma(C_3, C_5)$, and $C_\delta(C_4)$ carbon atoms of each conformer is possible. This assignment is based on the integrated intensities, the analysis of the dynamic broadening of individual spectral lines, the employment of other recording techniques, as well as literature data for chloro-substituted hydrocarbons[27]. Only four signals are observed in the spectrum obtained at 273 K, which indicates the rapid inversion of the ring in chlorocyclohexane. The assignment of the spectra lines measured at 273 K follows from the assignment of the signals in the low-temperature spectrum but it can also be based on independent data[28].

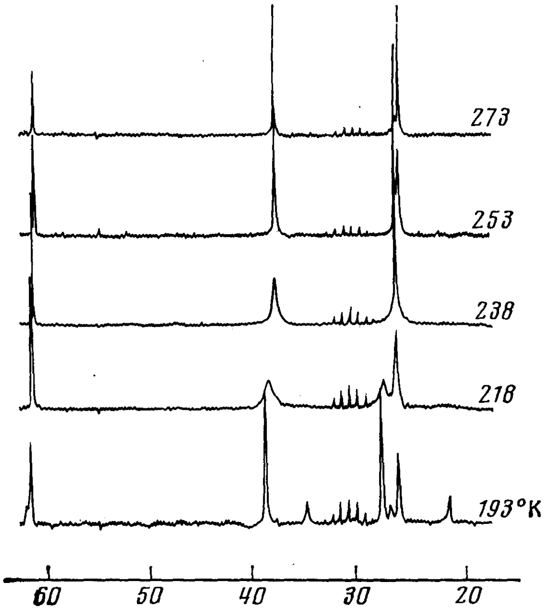


Figure 1. ^{13}C NMR spectra of chlorocyclohexane with complete proton coupling. The lower-intensity signals in the low-temperature spectrum refer to the axial conformer. The multiplet in the region of 30 p.p.m. is the signal of deuteroacetone used as the reference signal.

In conformity with the problems described above, it is possible to arrange systematically in the following manner the information which follows from the temperature-dependent ^{13}C NMR spectra.

1. Conformational Analysis

The number of conformers may be determined from spectra measured at 173–193 K. Using the integrated intensities *I* of the signals of the individual conformers A_1 and A_2, one can determine the equilibrium constant *K*:

$$a_i = I_2/I_1 = K, \qquad (7)$$

where subscript *i* corresponds to the *i*th pair of carbon atoms. The concentrations of individual conformers may be determined from the spectra measured at room temperature using the following equation for the spectral parameter averaged with respect to the conformers:

$$\langle\theta\rangle=\sum_i p_i\theta_i=p_1\theta_1+p_2\theta_2, \tag{8}$$

where the chemical shifts δ or the spin–spin coupling constants J may be used as θ.

2. Dynamics of Ring Inversion

Using the parameters of the line form in the NMR spectra in the regions corresponding to intermediate exchange and the well developed procedures for the treatment of such temperature-dependent spectra[21-23], it is possible to determine the rate constants k_{ae} and k_{ea}. If such measurements are carried out over a wide range of temperatures, the activation parameters for the process can be found: $\Delta G^{\neq}$, $\Delta H^{\neq}$, and $\Delta S^{\neq}$.

3. Chemical Shifts and the Spin–Spin Coupling Constants

The chemical shifts of the ^{13}C NMR signals of the individual conformers, δ_i^1 and δ_t^2, can be determined from spectra measured at 173–193 K. If the test compound contains other magnetic nuclei (^{19}F, ^{31}P, etc.) then information about the spin–spin ^{13}C–X coupling constant (where X is the ^{19}F, ^{31}P, etc. isotope) may be derived from ^{13}C NMR spectra under the conditions of complete decoupling from protons. Unfortunately it is so far impossible to obtain information about the $J(^{13}C-^{1}H)$ constants, which is due to the difficulties in the recording and analysis of monoresonance ^{13}C NMR spectra. Definite advances have been achieved in recent years in the analysis of monoresonance ^{13}C NMR spectra of certain types of organic compounds[29]. This suggests that eventually it will be possible to use information about the $J(^{13}C-^{1}H)$ constants also for substituted cyclohexanes, which is of significant stereochemical interest.

The ^{13}C NMR method suffers from certain limitations.

(a) Limitations due to the low value of the "signal/noise" ratio. Despite the advances towards an increase of sensitivity achieved in recent years as a result of the introduction of pulsed FT,[30] the problem of sensitivity in the measurement of ^{13}C NMR spectra remains extremely urgent. In particular, each spectrum illustrated in Fig. 1 required the accumulation of ~1000 pulses for a solution concentration of about 30 wt.%. With overall 10 s intervals between the pulses, the recording of each spectrum required ~3 h. Reduction of the solution concentration by a factor of 2 would entail an increase in the time required for the experiment by a factor of 4. This factor precludes studies on sparingly soluble substances.

(b) Limitations due to the distortions of signal form. When ^{13}C NMR spectra are recorded under the conditions of complete decoupling from protons using pulsed methods (FT), the NMR signal form (particularly the integrated intensity) may be distorted by a number of factors. The most important of these are (1) the non-identical increase of the intensities of the signals due to different ^{13}C nuclei owing to the different values of the NOE factors, (2) signal saturation arising as a consequence of unduly short periods of pulse repetition, (3) errors introduced by the limited power of the computer, and (4) other sources of apparatus error associated with the presence of lateral signals due to rotation, the contribution of dispersion to the recorded signal, the frequency dependence of the signal intensity, and the influence of the inhomogeneity of the exciting field $\dot{\gamma}H_1$ ($\dot{\gamma}=\gamma/2\pi$, γ being the gyromagnetic constant). A more detailed analysis of these factors may be found in the papers by Freeman and Hill[31] and by Jones and Sternlicht[32].

(c) Limitations associated with the necessity for the complete assignment of the spectrum. ^{13}C NMR spectra with complete decoupling from protons show only singlet lines due to non-equivalent carbon atoms. Although in many instances the assignment of the lines is fairly evident, in practice, for example in the analysis of complex mixtures, the problem of the assignment of the lines is not trivial. Various methods have been described for the assignment of spectral lines using modifications of $^{13}C-\{^{1}H\}$ double resonance[34], additive schemes for the calculation of ^{13}C chemical shifts[25,27], spin–lattice relaxation times for ^{13}C nuclei (T_1),[35,69] and induced shifts resulting from the addition of paramagnetic shift reagents have been described[20]. Although the use of these methods does increase the total amount of work which must be performed in the investigation, it results, in principle, in the solution of the assignment problem in almost all cases.

Analysis of the scope and limitations of the ^{13}C NMR method have shown that in principle the method can be used to solve all the problems formulated above. An important limitation concerns the study of the influence of the medium, because the measurement of ^{13}C NMR spectra in dilute solutions is difficult (certain data of this kind are described by Schneider and Freitag[33] and Pehk et al.[36]). Studies on substituted cyclohexanes have so far been made only in concentrated solutions. The problem of the investigation of the properties of individual conformers within the framework of ^{13}C NMR spectroscopy naturally reduces merely to the interpretation of the information which follows from the NMR spectra, i.e. the chemical shift of the ^{13}C nuclei and the spin–spin coupling constants involving such nuclei. Furthermore, useful information about the correlation times for molecular motion can be obtained by measuring the spin–lattice relaxation times and NOE factors.

IV. CONFORMATIONAL ANALYSIS USING ^{13}C NMR

1. TEMPERATURE RANGE

The experimental data available at the present time have shown that the accuracy of the measurement of the conformational equilibrium constant K is to a large extent determined by the temperature range employed. The following characteristic temperature ranges can be distinguished for NMR spectroscopy.

Temperatures Below 173 K

In this temperature range ring inversion becomes very slow (here and henceforth we are considering the NMR time (scale), so that the signals of the individual conformers should be observed. However, owing to experimental difficulties (the choice of solvent, the establishment of a high concentration in the solution, and the design characteristics of the transducers), studies in this temperature range have not so far been made with the aid of ^{13}C NMR.

Temperatures in the Range 173–193 K

Here ring inversion is slow and the signals of individual conformers are observed. They are adequately resolved, which permits correct integration and determination of the equilibrium constant.

Temperatures in the Range 193–243 K

An intermediate rate of inversion obtains. This leads to a significant broadening of the spectral lines and their overlapping (Fig. 1), which prevents the separate integration of the signals due to the conformers. The study of conformational equilibrium in this temperature range requires prolonged experiments with calculation of the total spectral line form. It is perhaps possible to quote only one example of a fairly thorough analysis of spectra in this temperature range carried out by Bovey et al.[37] for the inversion of fluorocyclohexane (joint analysis of ^{19}F and ^{1}H NMR spectra).

Temperatures above 243 K

Ring inversion is rapid and the ^{13}C NMR spectra show averaged signals. This temperature range is of particular interest, since it includes room temperature—the most important for practical purposes. The ratio of the concentrations of the conformers p_1 and p_2 may be estimated by Eqn. (8). It must be emphasised that there are many specific problems which significantly hinder the use of equations for the average parameters (see the reviews of Jensen and Bushweller[15] and Garbish[36]). Such estimates frequently lead to a decrease of the accuracy of the calculated equilibrium constants or in general to doubtful and contradictory results.

2. ASSIGNMENT OF THE SPECTRAL LINES

In conformational analysis the correct assignment of the spectral lines is of greatest importance. The assignment procedure presents no difficulties, provided that the chemical shifts of non-equivalent carbon atoms differ by more than 2–3 p.p.m. For the correct assignment of the lines in the spectra of monosubstituted compounds, it is sufficient to use symmetry considerations, integrated signal intensities, and data concerning the influence of the substituent on the chemical shift of the ^{13}C nuclei in model saturated hydrocarbons[39-42]. An extremely effective procedure for the assignment of the lines of polysubstituted compounds, involves the comparison of the experimental shifts with calculated additive data[43-45]. Among the special assignment methods useful for the analysis of the spectra of substituted cyclohexane, mention should be made of the procedure based on the study of the dynamic broadening of the spectral lines, which permits the identification of the signals due to pairs of nuclei undergoing exchange. One should also note that the employment of integrated intensities should be approached with a certain amount of caution, because incorrectly selected conditions for the recording of the spectrum in pulsed FT may lead to considerable distortions of the signal intensities up to the disappearance of certain signals from the spectrum.

3. EQUILIBRIUM BETWEEN THE CONFORMERS AT TEMPERATURES IN THE RANGE 173–193 K

The constant K for the equilibrium between two conformers A_1 and A_2 of a substituted cyclohexane is determined from the integrated signal intensities in low-temperature spectra. Since several ^{13}C signals are observed for each conformer (six in the general case), there is a possibility of averaging with respect to the corresponding pairs of signals:

$$K = \frac{1}{N}\sum_{i=1}^{N} \alpha_i. \tag{9}$$

The problem of the accuracy of the measurement of the conformational equilibrium constants is of significant interest for conformational analysis. Since the integrated intensities are influenced by many distortions, the problem of the errors of the measurements requires special examination. Subject to certain simplifying assumptions, the ratio of the integrated intensities of two signals in the spectrum (for pulsed FT) is related to the required quantity $K = p_2/p_1 = M^{\mathrm{i}}_{\mathrm{Z},2}/M^{\mathrm{i}}_{\mathrm{Z},1}$, where M_{Z} is the projection of the nuclear magnetisation vector onto the z axis) by the expression

$$\alpha_i = \frac{I_i^2}{I_i^1} = \frac{(\eta(C_i^2)+1)}{(\eta(C_i^1)+1)} \cdot \frac{[1-\exp(-t/T_1(C_i^2))]}{[1-\exp(-t/T_1(C_i^1))]} \cdot K, \tag{10}$$

where the first term takes into account the difference between the Nuclear Overhauser effects for the ith pair of signals C^1_{i} and C^2_{i}, while the second term defines the difference between the saturation factors for the same signals[31,32]; $\eta = \mathrm{NOE} - 1 = I_{\mathrm{p}}/I_0 - 1$, where I_{p} and I_0 are the integrated signal intensities with and without proton decoupling respectively. The correct employment of Eqn. (10) for quantitative analysis thus requires data for NOE factors and the spin-lattice relaxation times $T_1(^{13}C)$. The time t in Eqn. (10) corresponds to the total interval between the pulses, equal to the sum of the sampling time of the free induction signal and the arrest time[4]. Technical difficulties in the measurement of NOE and of the relaxation time T_1 constitute serious obstacles to the use of ^{13}C NMR data in quantitative analysis. More detailed analysis shows[39,46,50,80] that the relaxation times of protonated carbon atoms (i.e. atoms forming part of methylidyne and methylene groups) are almost fully determined by the dipole–dipole mechanism and the NOE factors for such nuclei are therefore close to the theoretical value of 2.99.[3,4] There are also data showing that the relaxation times of the ^{13}C nuclei of substituted cyclohexanes do not exceed 3 s at 1733–193 K.[69] Hence it follows, in particular, that the distortions due to the differences between the relaxation times may be significantly reduced by using intervals of 8–10 s between the pulses. The accuracy of the measurement of the equilibrium constant K also depends on the value of the latter, the errors being a minimum for almost degenerate equilibria and increasing almost linearly with increase of K. Despite the fact that in most cases the correct analysis of the errors has not been carried out, presumably in real systems it is very difficult to achieve an accuracy better than to within 10%.

The results of a study of the conformational equilibria for a series of monosubstituted cyclohexanes at 163 to 204 K are presented in Table 1. It follows from these results that the standard relative error $\Delta\Delta G^\circ/\Delta G^\circ$ of the conformational energies in the range −0.3–1.8 kcal mole^{-1} is about 10%. The ^{13}C NMR data can be compared with those of Jensen and Bushweller[15] ("best" A-values)

(Fig. 2). Evidently the results obtained by these two methods of measurement of conformational energies are correlated, but the conformational energies found from ^{13}C NMR spectra are systematically higher by 20% than the values derived from ^{1}H NMR spectra. These discrepancies may be caused, particularly, by the fact that ^{13}C NMR measurements are made as a rule in much more concentrated solutions than those used for the measurement of low-temperature ^{1}H NMR spectra. The discrepancies are largest for $X = F$ (37%) and $X = OCH_3$ (36%). The problem of the true causes of these discrepancies is still obscure and requires a more detailed analysis of the errors of both methods.

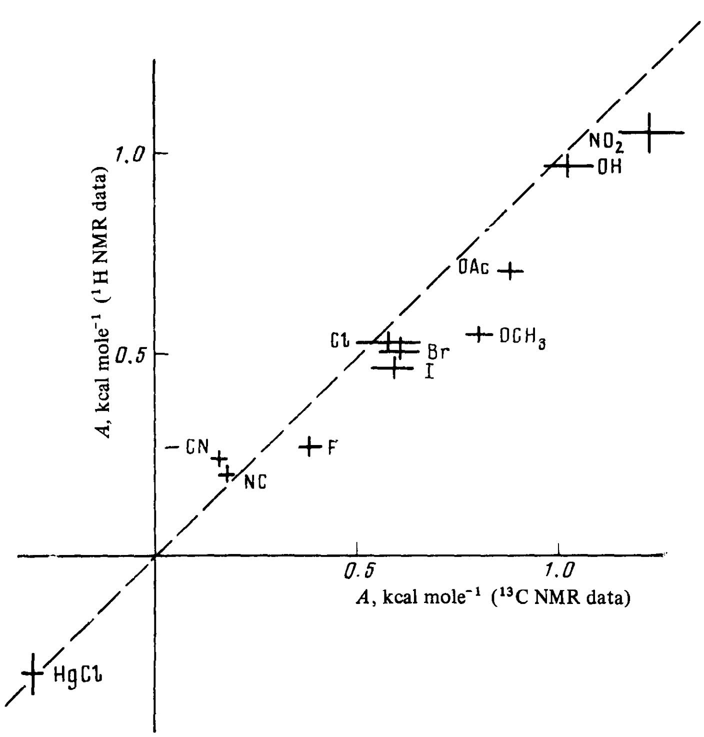


Figure 2. Comparison of the conformational energies obtained with the aid of ^{13}C and ^{1}H NMR for certain substituents in monosubstituted cyclohexanes.

Despite the fact that the problem of the relative accuracies of different methods of measurement of conformational energies has not been finally elucidated, ^{13}C NMR has already permitted progress in several important cases. In particular, it has been possible to obtain for the first time spectroscopic evidence for the existence of the axial conformer of methylcyclohexane—the classical object of conformational analysis—and to measure $-\Delta G_{173°} = 1.8 \pm 0.1$ kcal mole^{-1}.[42] Previous attempts to solve this problem[51] were based on indirect reasoning and yielded significantly divergent values (ranging from 1.5 to 2.0 kcal mole^{-1}).[7,52] This and other examples (nitrocyclohexane, cyclohexanol[42]) have shown that ^{13}C NMR is the most suitable method for the investigation of high-energy conformations. Another example of the successful application of ^{13}C NMR is provided by the study of mercury-substituted cyclohexanes[49]. Earlier conformational analysis of these compounds was complicated by the difficulty of interpreting the ^{1}H NMR spectra[53]. When ^{13}C NMR was used, it was possible to assign the signals on the basis of the $J(^{13}C-^{199}Hg)$ constants[54] and to show that the axial conformer predominates ($-\Delta G_{183°} = -0.30$ kcal mole^{-1}). The mercury-substituted compounds constitute the only example of systems with the preferential axial orientation of the substituent in a series of monosubstituted cyclohexane derivatives. This stabilisation is probably due to weak coordinate bonds formed between the hydrogen atoms in the γ-positions and the mercury atom, with participation of vacant 5*d* orbitals. Presumably such "anomeric" effects can be observed also for other organometallic derivatives of cyclohexane[84] (see also Table 1).

The still limited data available for polysubstituted cyclohexane derivatives do not allow a detailed elucidation of the characteristics of the conformational equilibrium over a fairly wide range of conditions (temperature, solvent) and types of substituents. The most interesting results were obtained with the aid of ^{1}H NMR[19,55-57] and ^{19}F NMR [58,59] but these methods cannot be regarded as universal either.

The attempts to employ ^{13}C NMR to investigate polysubstituted cyclohexanes using integrated spectral intensities are still not numerous[45,60-63], but they clearly show that the method makes it possible to overcome successfully the difficulties associated with the isomeric purities of the test systems.

In considering the conformational equilibria involving disubstituted cyclohexanes it is useful to divide the equilibria into two types: (1) the equilibrium between the *aa*- and *ee*-conformers, which obtains in 1,2-*trans*-, 1,3-*cis*, and 1,4-*trans*-isomers; (2) the equilibrium between the *ae*- and *ea*-conformers in 1,1-, 1,2-*cis*-, 1,3-*trans*-, and 1,4-*cis*-isomers. When the substituents are the same, the conformational transformation of type (2) is degenerate, so that $\Delta G = 0$. The experimental conformational energies $A_{\text{exp}}(X, Y)$ for compounds of types (1) and (2) are listed in Tables 2 and 3 respectively. In addition, the tables list the conformational energies obtained by the additive approach. The additive conformational energy A_{add} can be represented as the sum (or difference) of the conformational energies of both substituents, i.e.

$$A_{\text{add}}(X, Y) = A(X) + A(Y) \quad (\text{for } aa \rightleftharpoons ee), \tag{11}$$
$$A_{\text{add}}(X, Y) = A(X) - A(Y) \quad (\text{for } ae \rightleftharpoons ea).$$

The data quoted in Table 1 may be used as the A-values for specific substituents. The factors R, which are a measure of conformational non-additivity, may be determined from the experimental values of $A_{\text{exp}}(X, Y) = -\Delta G°(X, Y)$ and the calculated values of A_{add}:

$$R = A_{\text{add}}(X, Y) - A_{\text{exp}}(X, Y). \tag{12}$$

The following features may be deduced from the results (see also other studies[15,59] where other methods were used).

1. The *ee*-form is destabilised in the presence of bulky substituents (Br, Cl, CH$_3$), in *trans*-1,2-isomers (or the *aa*-form undergoes additional stabilisation), the destabilisation factor varying from 0.1 kcal mole^{-1} (for fluoroiodocyclohexane[59]) to 2 kcal mole^{-1} (for di-iodocyclohexane[64]); it probably increases with increase of the bulk of the substituent.

Table 1. Comparison of the conformational energies ($-\Delta G^0$) for monosubstituted cyclohexanes obtained from ^{13}C and ^1H NMR data*.

Substituent	^{13}C NMR				^1H NMR			
	solvent	T, K	$-\Delta G^0$, kcal mole^{-1}	Refs.	solvent	T, K	$-\Delta G^0$, kcal mole^{-1}	References
$HgOCOCH_3$	$CDCl_3$	183	-0.30 ± 0.03	49	$CDCl_3$	183	-0.30 ± 0.05	49
$HgOCOCH_3$	—	—	—	—	CS_2	193	0.61	15
CN	CF_2Cl_2	190	0.152 ± 0.005	40	CS_2	194	0.24 ± 0.003	15,53
NC	CF_2Cl_2	180	0.182 ± 0.015	40	CS_2	193	0.21 ± 0.013	15,53
F	CS_2	183	0.380 ± 0.03	39	CS_2	187	0.276 ± 0 02	15,53,37
F	CF_2Cl_2	180	0.360 ± 0.025	40	—	—	—	—
Cl	CS_2	193	0.53 ± 0.05	39	CS_2	192	0.528 ± 0.02	15,53
Cl	CF_2Cl_2	180	0.62 ± 0.04	40	—	—	—	—
Br	CS_2	198	0.61 ± 0.05	39	CS_2	192	0.476 ± 0.02	15,53
Br	CF_2Cl_2	200	0.585 ± 0.025	40	—	—	—	—
I	CS_2	195	0.59 ± 0.05	39	CS_2	193	0.468 ± 0.02	15,53
I	CF_2Cl_2	180	0.455 ± 0.025	40	—	—	—	—
$Pb(CH_3)_3$	CD_2Cl_2	204	0.67 ± 0.06	84	—	—	—	—
OCH_3	CF_2Cl_2	180	0.75 ± 0.035	40	CS_2	191	0.547 ± 0.019**	15,53
$OSi(CH_3)_3$	CF_2Cl_2	170	0.735 ± 0.015	48	—	—	—	—
$OCOCH_3$	CF_2Cl_2	180	0.885 ± 0.03	40	CS_2	185	0.71 ± 0.05	15,53
OH	CS_2	183	1.02 ± 0.1	42	CS_2	190	0.97	15,53
OH	CF_2Cl_2	180	>1.4	40	—	—	—	—
$Sn(CH_3)_3$	CD_2Cl_2	204	1.06 ± 0.14	84	—	—	—	—
NO_2	CS_2	183	1.27 ± 0.2	42	CS_2	183	1.05 ± 0.14	15,53
CH_3	pure compound	163	1.6	41	—	—	—	—
CH_3	CS_2	173	1.80 ± 0.1	42	—	—	—	—
CH_3	$CFCl_3-CDCl_3$	172	1.74 ± 0.06	106	—	—	—	—

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*The low-temperature NMR spectra; the method of integrated intensities was used [Eqns. (3) and (7)].

**Data for the OCD_3 substituent.

2. The diaxial form of *cis*-1,3-isomers is exceptionally unfavourable as a result of 1,3-*syn*-diaxial interactions of the bulky substituents. Theoretical estimates for such interactions have been carried out by Bailey et al.[57] in relation to the *syn*-diaxial interaction of the methyl group and fluorine, chlorine, bromine, or iodine atoms. The calculated energies of these interactions, amounting to 0.34, 7.34, 15.07, or 28.37 kcal mole^{-1} respectively (the calculations were performed with the aid of the Hill potential[65]), show that the repulsion energy for the substituent increases with increasing bulk of the latter, causing the destabilisation of the diaxial conformer.

Table 2. Equilibria of the type $aa \rightleftharpoons ee$ for disubstituted cyclohexanes according to ^{13}C NMR data (173–193 K)*.

Compound	$A_{exp}(X, Y)$, kcal mole^{-1}	$A^{**}_{add}(X, Y)$, kcal mole^{-1}	R, kcal mole^{-1}	References
trans-1,2-Dichlorocyclohexane	0.34	1.06	0.72	61
trans-1,2-Dichlorocyclohexane	0.47***	1.06	0.69	45
cis-1,3-Dichlorocyclohexane	>1.5***	1.06	<−0.50	45
trans-1,4-Dichlorocyclohexane	0.03***	1.06	1.03	45
trans-1,2-Dibromocyclohexane	−0.76	1.22	1.98	61
trans-1-Chloro-2-methoxycyclohexane	0.29	1.28	0.99	61
trans-1-Bromo-2-methoxycyclohexane	0.48	1.36	0.88	61
trans-1-Hydroxy-2-methoxycyclohexane	1.05	1.77	0.72	61
trans-1-Hydroxy-2-methylcyclohexane	>1.4	2.8	<1.4	62
trans-1-Hydroxy-4-methylcyclohexane	≥1.4	2.8	≤1.4	62
cis-1-Hydroxy-3-methylcyclohexane	>1.4	2.8	<1.4	62

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*For solutions in CS_2; method of integrated intensities.

**The conformational energies obtained from ^{13}C NMR spectra were used in the calculation of A_{add} (see Table 1).

***For a mixture of isomers of *trans*-1,2-, *cis*-1,3-, and *trans*-1,4-dichlorocyclohexanes.

3. The *aa*-form of *trans*-1,4-isomers undergoes additional stabilisation ($R_{14} > 0$). An attempt at a theoretical explanation of this effect, based on the consideration of the energy of the electrostatic interaction in 1,4-dihalogenocyclohexanes, has been made[19].

Table 3. Equilibrium of the type $ae \rightleftharpoons ea$ for disubstituted cyclohexanes according to ^{13}C NMR data (173–193 K)*.

Compound	$A_{exp}(X, Y)$, kcal mole^{-1}	$A^{**}_{add}(X, Y)$, kcal mole^{-1}	R, kcal mole^{-1}
cis-1-Hydroxy-4-methylcyclohexane	0.74	0.76	0.02
trans-1-Hydroxy-3-methylcyclohexane	0.94	0.76	−0.18
cis-1-Hydroxy-2-methylcyclohexane	0.53	0.76	0.23

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*Method of integrated intensities[62] (for solutions in CS_2).

**The conformational energies based on ^{13}C NMR data (for solutions in CS_2) were used in the calculation of $A_{add}(X, Y)$.

4. The deviations from additivity for 1,4-*cis*-, 1,3-*trans*-, and 1,2-*cis*-isomers involved in transformations of the $ea \rightleftharpoons ae$ type are comparatively small (the values of R are $\sim\pm0.2$ kcal mole^{-1}) and on the whole the additive scheme can be used to predict the conformational composition of such isomers.

The conformational equilibria of polysubstituted (three and more substituents) cyclohexanes have not been investigated so far by ^{13}C NMR in the range 173–193 K. It is to be expected that the method will find applications in the immediate future in the study of these and related systems (decalins, tetralins, steroids, etc.)

4. CONFORMATIONAL EQUILIBRIUM AT TEMPERATURES NEAR 300 K

In the high-temperature region the equilibrium parameters are determined using the equation for average parameters [Eqn. (8)]. If it is assumed that only two conformers are involved in the equilibrium (the equatorial and axial conformers in the case of monosubstituted cyclohexanes), then it follows from Eqn. (8) that

$$p_2 = \frac{\langle\theta\rangle_i - \theta_i^2}{\theta_i^2 - \theta_i^1} \qquad (13)$$

and

$$K = \frac{\langle\theta\rangle_i - \theta_i^1}{\theta_i^2 - \langle\theta\rangle_i}. \qquad (14)$$

Thus, provided that the spectroscopic parameters θ_i^1 and θ_i^2 are known under stereochemically rigid conditions, it is possible to determine from the average value the fractions of the conformers and the equilibrium constants.

It is noteworthy that the problem of the interpretation of the averaged spectroscopic parameters measured at temperatures ensuring a rapid conformational transformation is of general interest for the conformational analysis of organic compounds. This is due to the fact that in many systems which are of interest as regards their conformations[12,13] (cyclopentanes, cycloheptanes, cyclohexanones, dioxans, piperidines, etc.) it is extremely difficult to create conditions sufficient to "freeze out" individual conformations. In systems of this kind this requires measurements at temperatures in the range 123–173 K, which is not always possible. This fact explains the great interest in the interpretation of averaged spectroscopic parameters in terms of conformational equilibria[66]. The available reviews on the application of the method of averaged parameters (substituted cyclohexanes[13,15], rotational isomers of ethane-like molecules[38,67]) show that this method of studying equilibria should be used with much caution. The fundamental difficulties make it necessary to take into account the temperature dependence of the spectroscopic parameters of rigid systems. This implies that in principle one cannot use in Eqns. (13) and (14) the parameters θ_i^a and θ_i^e obtained from low-temperature measurements.

In describing the results of the application of the method of averaged parameters to substituted cyclohexanes, it is useful to consider separately the chemical shift data and the spin–spin coupling constants. The former are of considerable practical interest, since they can be measured in all cases. On the other hand, the use of averaged spin–spin coupling constants (in those cases where the relevant data may be determined from the spectrum) apparently leads to more accurate results, because according to some data[66] the constants are less affected by temperature.

Eqns. (13) and (14) can be used in two ways[62]. One of them, which may be called experimental, involves the use as θ_i^e and θ_i^a of the experimental chemical shifts of the ^{13}C nuclei of individual conformers obtained from spectra measured at 173–193 K. In principle, the method can be modified by studying experimentally the temperature dependence of the chemical shifts in the accessible temperature range (123–200 K) and extrapolating the relation obtained to higher temperatures. However, ^{13}C NMR studies of this kind have not so far been made and the chemical shifts δ_i^e and δ_i^a were assumed to be independent of temperature, which probably introduced a systematic error. The second way of using Eqns. (13) and (14), which may be referred to as the computational procedure, consists in using the chemical shifts calculated in accordance with some scheme; different empirical and semiempirical methods may be used in the calculation. The evident requirement which must be met by the computational scheme is that the calculated chemical shifts should be sufficiently accurate. The required level of accuracy ($\Delta\delta$) follows directly from Eqns. (13) and (14): the error must be significantly less than the range of variation of the shift, i.e. $\Delta\delta < |\delta_i^e - \delta_i^a|$.

A satisfactory computational scheme for the calculation of chemical shifts has not so far been proposed for monosubstituted cyclohexanes and the experimental method was therefore used in the study of the conformational equilibria at 300 K.[39] The only attempt to employ the computational method, undertaken by Pehk and Lippmaa[28], involved the use of the chemical shifts for the corresponding t-butyl derivatives $(CH_3)_2XCH$.[4-6] When the chemical shifts of the conformers cannot be measured experimentally at low temperatures (for example, owing to the limited solubility of the corresponding monosubstituted compound), this procedure is the only one available for the estimation of the equilibrium constant. However, the analogy with the t-butyl derivatives is probably extremely approximate and the method can be recommended only for qualitative estimates.

Table 4. Parameters of the conformational equilibria for halogenocyclohexanes at 298 K according to ^{13}C NMR chemical shifts and their comparison with the results obtained by other methods.

Halogen	Parameter	Position of carbon atom				^{13}C NMR	Results obtained by other methods**	
		α	β	γ	δ	$\langle p_e\rangle$	p_e	method
F	δ*	63.29	4.82	−4.76	−2.25			
	p_e	0.67	0.73	0.64	0.30	0.65	0.57	^{19}F NMR
	f_i	0.22	0.19	0.23	0.01			
Cl	δ	32.24	9.68	−2.09	−1.60			
	p_e	3.00	0.75	0.70	0.75	0.79	0.73	^1H NMR
	f_i	0.09	0.25	0.40	0.05			
Br	δ	25.06	10.51	−1.02	−1.42			
	p_e	1.00	0.68	0.65	1.00	0.74	0.72	^1H NMR
	f_i	0.22	0.25	0.47	0.06			
I	δ	4.38	12.52	0.40	−1.40			
	p_e	0.91	0.80	0.71	0.65	0.80	—	—
	f_i	0.40	0.23	0.33	0.04			

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*The chemical shifts are expressed in p.p.m. relative to C_6H_{12} (from the paper by Subbotin and Sergeyev[39]).

**Taken mainly from Squillacote et al.[18] (see also Refs. 53 and 37).

Both the averaged chemical shifts (see also Table 4) and the shifts of the individual conformers (see Table 11) of many monosubstituted cyclohexanes are known[39-42], which makes it possible to examine the problem of the applicability of the experimental method to the study of the conformational equilibrium at 298 K. The corresponding results are presented in Table 4 for halogenocyclohexanes.

In the calculation of the fraction of the equatorial conformer p_e by Eqn. (13) the experimental chemical shifts of the ith carbon atoms ($i = \alpha$, β, γ, or δ) taken from Subbotin and Sergeyev[39] were used for the a- and e-conformers. Table 4 presents for comparison the fractions of the equatorial conformer obtained from results found by other methods (^{1}H NMR and ^{19}F NMR) using an analogous procedure[15].

It follows from the data in Table 4 that the values of p_e corresponding to different atoms are significantly scattered. In certain cases absurd results ($p_e > 1$) are obtained. The above deficiencies are a consequence of the temperature dependence of the chemical shifts of the individual conformers. The available estimates of the influence of temperature on the chemical shifts of individual substances quoted in the literature have shown[68-70] that the "temperature coefficients" may reach 1 p.p.m. per 100°C. The experimental method for the investigation of high-temperature equilibria is therefore ineffective when the difference between the chemical shifts of the ith atoms of the conformers is small (1 p.p.m. and less). In particular, this is characteristic of the δ-carbon atoms in monosubstituted cyclohexanes.

The error in the calculation in accordance with this scheme may be reduced by several formal procedures. Firstly, it is possible to exclude from consideration the results to which correspond relatively small differences $|\delta_i^e - \delta_i^a|$. Secondly, in the calculation of the average value it is possible to introduce "statistical weights" for the results of individual measurements[62]:

$$\langle p_e\rangle = \sum_i f_i p_e^i \tag{15}$$

where

$$f_i = \frac{|\delta_i^e - \delta_i^a|}{\sum\limits_{i=1}^{N} |\delta_i^e - \delta_i^a|} \tag{16}$$

is the "statistical weight" of p_e^i.

In this procedure more reliable estimates of p_e^i, obtained for larger differences $|\delta_i^e - \delta_i^a|$, have a larger statistical weight and formally one can permit the inclusion of results leading to $p > 1$ or $p < 0$. Data obtained by this method are in reasonable agreement with literature estimates (see Table 4). For polysubstituted compounds, the computational as well as the experimental method may be used to measure the constant K and the additive values of the chemical shifts of the conformers may be used as the calculated values.

Both methods for the investigation of the high-temperature equilibria based on calculations in accordance with an additive scheme have been used to investigate the conformations of isomeric methylcyclohexanols[62]. It follows from the data in Table 5 that the two methods give similar results. The conformer with the equatorial orientation of the methyl group (the ea-conformer in terms of the notation of Subbotin et al.[62]) predominates in all cases. The fraction of this conformer is a minimum for the 1,2-*cis*-isomer and a maximum for the 1,3-*trans*-isomer. The above tendency has been confirmed by low-temperature measurements (Table 5).

As regards the use of spin–spin coupling constants in the study of high-temperature equilibria, we may note that the experimental data available hitherto are extremely limited and refer mainly to fluorinated cyclohexanes[39,71], i.e. consist of $J(^{13}C-^{19}F)$ constants. By analogy with averaged chemical shifts, here too it is possible to distinguish two procedures for the interpretation of the results, but, since a satisfactory scheme for the calculation of spin–spin coupling constants does not yet exist, only the experimental procedure has so far been tested. Constants for the spin–spin coupling of the ^{19}F nuclei with all the non-equivalent ^{13}C nuclei of fluorocyclohexane have been found for both conformers at 183 K as well as the average spin–spin coupling constants at 300 K. These data can be used in Eqn. (14) to estimate the fraction of the equatorial conformer at 300 K, as was done in the analysis of the chemical shift (i.e. the "statistical weights" of the individual measurements are introduced) (Table 6).

Table 5. The fraction of the dominant conformer $\langle p_e\rangle$ in isomeric methylcyclohexanols (according to the conformationally averaged ^{13}C NMR chemical shifts at 300 K [62]).

Compound	$\langle p_e\rangle_{exp}$	$\langle p_e\rangle_{calc}$	$p_e^{l.t.*}$
cis-1-Hydroxy-2-methylcyclohexane	0.74	0.84	0.81
trans-1-Hydroxy-3-methylcyclohexane	0.83	0.96	0,93
cis-1-Hydroxy-4-methylcyclohexane	0.81	0.85	0,88

*Obtained from low-temperature ^{13}C NMR spectra by measuring the integrated signal intensities for the individual conformers.

Table 6. The spin–spin coupling constants $J(^{13}C-^{19}F)$ for fluorocyclohexane at 300 K and the fractions of the equatorial conformer.

Parameter	Position of carbon atom			
	α	β	γ	δ
$J(^{13}C-^{19}F)$, HZ	170.6	19.0	7.6	1.5
p_e^*	0.69	0.66	0.64	0.50
f_i	0.26	0.20	0.51	0.05

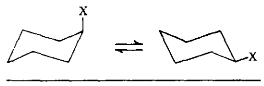
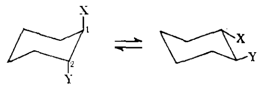
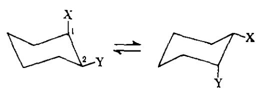
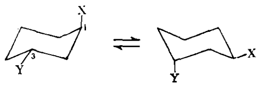
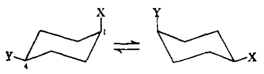
*The value averaged with respect to the positions of the carbon atom is $\langle p\rangle = 0.66$.

The average fraction of the equatorial conformer thus obtained (0.66) agrees with the value found from the chemical shifts (0.65; Table 4). Since the spin–spin coupling constants are less influenced by factors such as temperature and the solvent, one may expect their successful application in conformational analysis.

5. ENTHALPIES AND ENTROPIES OF THE REVERSIBLE CONFORMATIONAL TRANSFORMATION ACCORDING TO ^{13}C NMR DATA

From the theoretical standpoint, the enthalpy $\Delta H°$ and entropy $\Delta S°$ of the conformational transformation are of greatest interest rather than its free energy ΔG_T° because these quantities are related to the structures of the conformers. However, their experimental determination is extremely difficult, because it requires the measurement of the equilibrium constants over a very wide temperature range. The experimental data on this problem are extremely fragmentary[15] and have not been subjected to a critical analysis. Since ^{13}C NMR permits measurements of the equilibrium constant K in two temperature ranges (173–193 K and in the vicinity of 300 K), attempts have been made to determine $\Delta H°$ and $\Delta S°$ from $\Delta G_{183°}$ and $\Delta G_{300°}$.[61,62] The results of these estimations for a series of substituted cyclohexanes are compiled in Table 7; however, one should note that, despite the relatively greater accuracy of the determination of $\Delta G°$ (on average to within 10–20% for $\Delta G°$—to within a quantity of the order of 0.5 kcal mole^{-1}), the enthalpies and entropies of the reversible conformational transformation determined from the difference of two ΔG°_{T} values at close temperatures are obtained with an accuracy to within ~0.3 kcal mole^{-1} and 1.5 e.u. respectively[72]. It follows from the analysis of the errors that the accuracy diminishes rapidly with increase of the equilibrium constant (for $K > 1$). It is therefore hardly useful to pose the question of the theoretical interpretation of the enthalpies and entropies of the reversible conformational transformation. At any rate, the available data (Table 7) show that the entropies of the transformation are as a rule in the range ±1 e.u. This implies that the qualitative interpretation of the temperature dependence of the conformational equilibrium may be based on the hypothesis that there is no entropy contribution.

Table 7. The conformational energies and the enthalpies and entropies of the reversible conformational transformations for a series of substituted cyclohexanes[61,62].

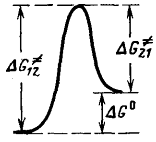
Inversion process	Substituent	$-\Delta G^0_{183°}$, kcal mole^{-1}	$-\Delta G^0_{300°}$, kcal mole^{-1}	$-\Delta H°$, kcal mole^{-1}	$-\Delta S°$, e.u.
	F	0.380	0.368	0.40	0.1
	Cl	0.530	0.790	0.02	—2.6
	Br	0.610	0.625	0.59	—0.1
	I	0.590	0.820	0.13	—2.3
	*trans*-1,2-(Cl, Cl)	0.34	0.19	0.61	1.4
	trans-1,2-(Br, Br)	—0.76	—0.51	—1.14	—2.0
	trans-1,2-(OCH$_3$, OH)	1.05	1.42	2.38	3.2
	trans-1,2-(OCH$_3$, Cl)	0.29	0.26	0.34	0.3
	trans-1,2-(OCH$_3$, Br)	0.48	0.37	0.67	1.0
	*cis*-1,2-(CH$_3$, OH)	0.53	0.62	0.40	0.75
	*trans*-1,3-(CH$_3$, OH)	0.94	0.94	0.94	0.0
	*cis*-1,4-(CH$_3$, OH)	0.74	0.86	0.56	—1.0

V. DYNAMICS OF RING INVERSION IN SUBSTITUTED CYCLOHEXANES

As already pointed out, the changes in the NMR spectrum occurring when the specimen temperature is altered (Fig. 1) may be used to analyse the dynamics of ring inversion (to solve this problem, it is necessary to find four activation parameters: the values of $\Delta H^{\neq}_{12}$ and $\Delta S^{\neq}_{12}$ characterising the transformation of the more stable conformer into a less stable one ($e \rightarrow a$ for monosubstituted cyclohexanes) and the values of $\Delta H^{\neq}_{21}$ and $\Delta S^{\neq}_{21}$ characterising the reverse process. Here we have

$$\Delta G^{\neq}_{12} = \Delta H^{\neq}_{12} - T\Delta S^{\neq}_{12}; \quad \Delta H^{\neq}_{12} = \Delta H^{\neq}_{21} - \Delta H^0;$$
$$\Delta G^{\neq}_{21} = \Delta H^{\neq}_{21} - T\Delta S^{\neq}_{21}; \quad \Delta S^{\neq}_{12} = \Delta S^{\neq}_{21} - \Delta S^0. \tag{17}$$

If the equilibrium parameters $\Delta H°$ and $\Delta S°$ are known, the problem reduces to determining two parameters (for example, $\Delta H^{\neq}_{12}$ and $\Delta S^{\neq}_{12}$; see the scheme below).



Before proceeding to the analysis of the results of the study of ring dynamics obtained with the aid of ^{13}C NMR, it is necessary to consider certain characteristics of the NMR method. In the first place we may note that the method is perhaps the only available procedure for the investigation of the dynamics of ring inversion in substituted cyclohexane. Data found by other methods are extremely limited (see, for example, Refs. 73 and 74) and have not been analysed critically. Among the different versions of the NMR method, ^1H NMR[55] and ^{19}F NMR[37,59] have become common. Studies by ^{19}F NMR are naturally restricted to fluorinated cyclohexanes (the so called method of the fluorine label proposed by Roberts[75]). When ^1H NMR is used, a fundamental difficulty arises because of the complex multiplet nature of the spectra due to the strong coupling between the spins in the spectra of substituted cyclohexanes. A correct interpretation of the dynamic effects requires in this case the use of the formalism of the density matrix[21,22]. The degrees of the systems of equations and the dimensions of the corresponding matrices obtained in this type of description increase rapidly with increase of the number of interacting spins. As a rule powerful computers must be used even for three spins, and, when there are five non-equivalent groups of interesting spins, the problem is virtually insoluble even when the best of modern computers are used. For certain special systems (for example, deuterated compounds), the degree of the systems of equations may be significantly reduced[76] but hitherto the formalism of the density matrix has not been used in studies on the dynamics of the inversion of cyclohexane derivatives.

It is also necessary to consider the general limitations in the study of the form of the potential surface for the ring inversion reaction by NMR. In examining these limitations one may begin with the phenomenological Bloch–McConnell equations for two-position exchange[23,77]. All inversions in substituted cyclohexanes belong to this type of exchange with two stable A_1 and A_2 states. Fig. 3 shows the region where NMR may be used to investigate two-position exchange (the shaded region). The limitations arise from the following considerations. Firstly, the modulus $|\Delta G^{\neq}_{12} - \Delta G^{\neq}_{21}|$ must not exceed 2 kcal mole^{-1}, which implies that the study of strongly displaced equilibria (or high-energy conformations) is difficult. Secondly, the values of $\Delta G^{\neq}_{12}$ and $\Delta G^{\neq}_{21}$ are limited from below by the low temperatures actually attained (6 kcal mole^{-1} for

120 K and 8 kcal mole^{-1} for 170 K). Thirdly, the limitations at the upper end are caused by the maximum attainable temperature in NMR transducers (473 K, which corresponds to ΔG = 24 kcal mole^{-1}). The region actually investigated proves to be even narrower, bearing in mind that the accuracy of the measurement of the dynamic broadening decreases rapidly with increase of the "degree of non-degeneracy" of the process. This fact reflects the real situation, which arises, in particular, in the study of substituted cyclohexanes. In fact the majority of the investigations of the dynamics of ring inversion by ^{1}H NMR [55,76,78] were devoted to degenerate systems. The inversion of non-degenerate systems has been studied using three models (fluorocyclohexane[37], 1,2-*trans*-fluoroiodocyclohexane[59], and 3-chloro-1,1-difluorocyclohexane[58]) by ^{19}F NMR. Some of the results obtained by ^{1}H and ^{19}F NMR are compiled in Tables 8 and 9.

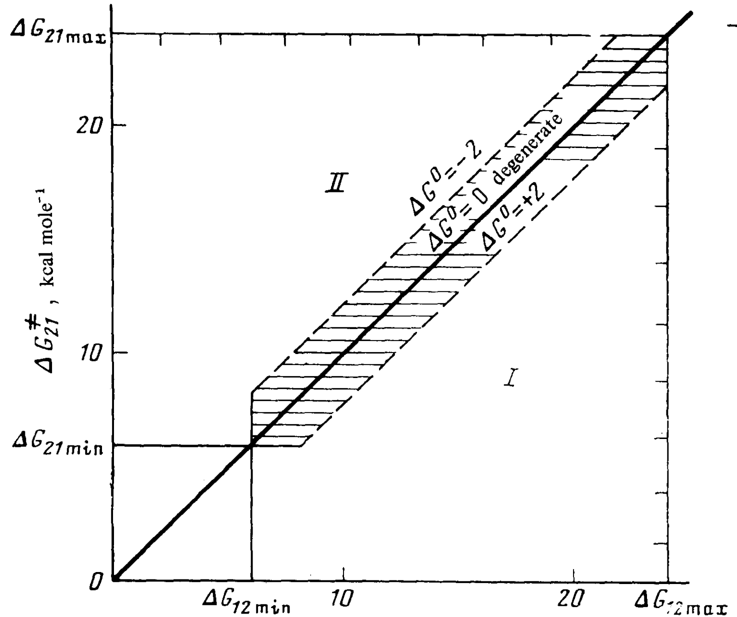
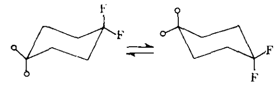
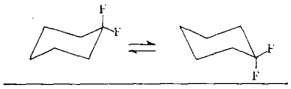
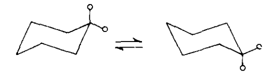
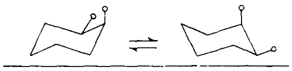
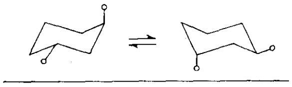
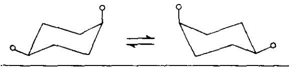
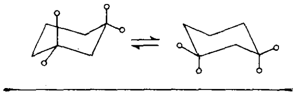
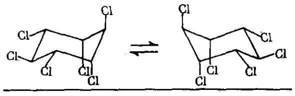


Figure 3. Energy diagram for the $(A_1) \rightleftharpoons (A_2)$ transformations. The values of $\Delta G_{\max}$ and $\Delta G_{\min}$ correspond to the maximum and minimum free energies of activation which can be measured by NMR; I—region where conformer A_1 predominates; II—region where conformer A_2 predominates.

^{13}C NMR also has many practical advantages over other versions of the NMR method in the study of intramolecular dynamic processes[27,81]. The most important advantage is that ^{13}C NMR spectra measured under the conditions of complete decoupling from protons do not contain spin multiplets and therefore permit the employment of a simpler formalism based on the Bloch–McConnell equation. The second advantage consists in a wider range of variation of the chemical shifts (exceeding by a factor of ~20 the range of the proton chemical shifts), which makes it possible, in principal, to carry out measurements on faster processes. However, one should note that studies on ring inversion processes in substituted cyclohexanes by ^{13}C NMR have so far been comparatively restricted and devoted mainly to degenerate processes (see Table 8). Non-degenerate inversion has been studied in only one instance, namely the inversion of chlorocyclohexane (see Table 9). In this last instance the prospects for the employment of ^{13}C NMR are so far extremely problematical. The data presented for degenerate processes undoubtedly show that the ^{13}C NMR method is more universal.

Table 8. The activation parameters for ring inversion in substituted cyclohexanes (the degenerate case).

Inversion process*	$\Delta G^{\neq}_{300°}$, kcal mole^{-1}	$\Delta H^{\neq}$, kcal mole^{-1}	$\Delta S^{\neq}$, e.u.	T_r, K**	NMR method	Refs.
	10.0	10.8±0.1	2.8±0.5	178	^{1}H—{^{2}H}	76
	10.5	8.9±0.5	−5.4±2	169	^{19}F	58
	9.5	10.4±0.4	3.0±2	170	^{19}F	58
	10.2	11.3±0.7	3.7±3	182	^{13}C—{^{1}H}	79
	10.3	9.3±0.7	−3.5±3	168	^{13}C—{^{1}H}	79
	9.8	11.1±0.7	4.5±3	178	^{13}C—{^{1}H}	79
	9.8	11.0±0.7	4.1±3	177	^{13}C—{^{1}H}	79
	10.4	6.4±0.2	−13.2±1	142	^{13}C—{^{1}H}	96
	12.2	9.9±0.6	−7.7±2.5	196	^{13}C—{^{1}H}	68

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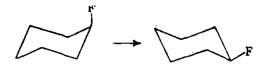
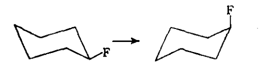
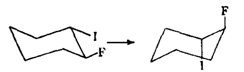
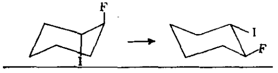
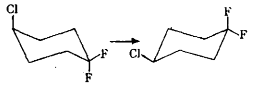
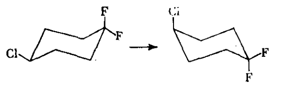
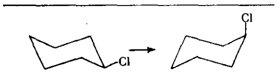
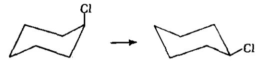
*The methyl group is designated by a circle.

**T_r is the temperature of stereochemical rigidity at which the rate of exchange is 1 s^{-1}. The values of T_r were determined from the approximate formula $T_r \simeq \Delta H/(\Delta S + 58.2)$, which follows from Eqn. (1) for $k = 1$ s^{-1}.

Despite the achievements in the experimental studies on inversion processes, a consistent method for the interpretation of these data has not so far been put forward in the literature. This is due to the general state of the theoretical description of the process under consideration[12,16,17]. The available estimates[17], carried out by Westheimer's method (a version of the method of atom–atom potentials) are in only qualitative agreement with experimental data and in all cases the accuracy of the latter is significantly higher than that of the calculation.

Table 9. The activation parameters for ring inversion in substituted cyclohexanes (the non-degenerate case).

Inversion process	$\Delta G^{\neq}_{300°}$, kcal mole^{-1}	$\Delta H^{\neq}$, kcal mole^{-1}	$\Delta S^{\neq}$, e.u.	Method	Refs.
	10.15	9.40	2.51	ЯМР	37
	10.32	9.87	−1.46	^{19}F	
	10.20	10.83	2.1	ЯМР	59
	9.54	10.17	2.1	^{19}F	
	9.8	10.2	1.4	ЯМР	58
	10.1	10.8	2.5	^{19}F	
	10.7	12.6±0.4	6.4±0.5	ЯМР	26
	11.4	13.0±0.4	5.3±0.5	^{13}C—{^{1}H}	

In view of the present lack of a quantitative theory of conformational transformations, many investigators are rightly interested in various approximate methods for the analysis of the inversion dynamics, which make it possible to establish the occurrence of ring inversion and to determine the approximate thermodynamic characteristics of this process. The free energies of activation, calculated directly from the rate constants defined by Eqn. (1) at a specified temperature, may be used as characteristics of this kind. Sometimes the specified temperature is the temperature of stereochemical rigidity T_r,[82] which is determined from the nature of the broadening of the lines in the slow exchange stage (T_r is the temperature at which the exchange rate constant is 1 s^{-1}). For degenerate inversions investigated by ^{13}C NMR, the values of T_r are listed in Table 8. One should note that T_r varies within wide limits (142–196 K). We may point out that quite recently it proved possible to establish with the aid of ^{13}C NMR that γ-hexamethyl-(*aeaeae*)-cyclohexane is rigid even at room temperature and undergoes inversion only on heating to 370 K; estimates of the free energy of activation gave 17.6 kcal mole^{-1}.[83] The ^{13}C NMR method is the most effective and universal procedure in the search for anomalous inversion barriers.

VI. CHEMICAL SHIFTS OF ^{13}C NMR NUCLEI IN INDIVIDUAL CONFORMERS OF SUBSTITUTED CYCLOHEXANES

In those cases where there are adequate grounds for the assumption that the conformational equilibrium is strongly displaced towards one conformer, it is possible to employ high-temperature spectroscopic data (for 300 K) as the individual spectroscopic characteristics of the dominant conformer. This approximation is valid for the majority of alkyl groups; the corresponding chemical shifts are listed in Table 10. However, in the general case where the nature of the conformational equilibrium is unknown, it is necessary to investigate low-temperature spectra. The relevant data for monosubstituted cyclohexanes are listed in Table 11. Data obtained by optimising the additive scheme for the determination of chemical shifts are quoted for the methyl group[44].

Table 10. ^{13}C NMR chemical shifts (δ, p.p.m.) in monosubstituted cyclohexanes $C_6H_{11}X$ (X is a substituent with a conformational energy ≥2 kcal mole^{-1}).

X	Position of carbon atom			
	α	β	γ	δ
C_2H_5	12.6	6.1	−0.5	−0.2
n-C_4H_9	10.8	6.5	−0.5	−0.3
t-C_4H_9	21.2	0.5	0.1	−0.5
C_6H_{11}	16.7	3.2	−0.2	−0.2
C_6H_5	17.5	7.3	−0.2	−0.9

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*Relative to cyclohexane (according to Pehk and Lippmaa[28])

In general, additive schemes for the compilation of ^{13}C chemical shifts have been widely used (see, for example, the selection of data in the review of Martin et al.[25]), particularly as one of the most effective methods for the assignment of spectral lines. Additive schemes are devised with the aid of a system of increments $\Delta_i(X)$, each of which characterises the influence of the substituent X on the shifts of the *i*th atom of the unsubstituted molecule. The index *i* describes the possible positions of a cyclohexane carbon atom relative to the substituent. Thus the ^{13}C NMR chemical shifts adjusted to the chemical shift of cyclohexane (27.50 p.p.m. relative to tetramethylsilane in terms of the δ-scale) can be regarded as the increments $\Delta_i(X)$.

Additive schemes for the calculation of ^{13}C NMR chemical shifts have been used successfully in the analysis of the spectra of dichlorocyclohexanes[46], methylcyclohexanols[62], a series of 1,2-disubstituted compounds[61], polymethylcyclohexanes[43], methyl derivatives of methylcyclohexanol[85], chloromethyl derivatives[86], etc. In most cases the deviations did not exceed 2 p.p.m. Appreciable upfield deviations (>2 p.p.m.) have been observed systematically in only one case—in the analysis of the shifts of the $C_{(1)}$ and $C_{(2)}$ atoms in 1,2-disubstituted compounds. The non-additivity of the shifts observed for 1,2-disubstituted cyclohexanes is probably general, because analogous deviations (sometimes referred to as the "*ortho*-effect") have been found also for other 1,2-disubstituted compounds: benzene[4], cyclopropane[87], ethylene[88], and cyclo-octane[99] derivatives. We may note that, for the diaxial orientation of the substituents, this effect is a maximum (Table 12). Thus the phenomenon is probably due to the overall influence of electronic and steric factors.

Table 11. The ^{13}C NMR chemical shifts (δ, p.p.m.) relative to C_6H_{12} for monosubstituted cyclohexanes.

X	δ, p.p.m.	Position of carbon atom				Solvent	Refs.
		α	β	γ	δ		
F	δ_i^e	64.38	5.53	−3.46	−2.57	CS_2	39
	δ_i^a	61.12	2.93	−7.11	−2.11		
	$\delta_i^a-\delta_i^e$	−3.26	−2.60	−3.65	0.46		
Cl	δ_i^e	32.80	10.62	−0.14	−1.81	CS_2	39
	δ_i^a	33.12	6.89	−6.61	−0.97		
	$\delta_i^a-\delta_i^e$	0.32	−3.73	−6.47	0.84		
Br	δ_i^e	25.13	11.75	1.35	−1.41	CS_2	39
	δ_i^a	28.35	7.90	−5.48	−0.55		
	$\delta_i^a-\delta_i^e$	3.22	−3.85	−6.83	0.86		
I	δ_i^e	3.64	13.40	2.28	−1.67	CS_2	39
	δ_i^a	11.30	9.04	−4.19	−0.89		
	$\delta_i^a-\delta_i^e$	7.66	−4.36	−6.47	0.88		
OH	δ_i^e	42.59	8.51	−1.65	−1.03	CS_2	42
	δ_i^a	37.92	5.28	−6.73	−0.61		
	$\delta_i^a-\delta_i^e$	−4.67	−3.23	−5.08	0.42		
OCH_3	δ_i^e	51.80	4.49	−2.80	−1.76	CF_2Cl_2	40
	δ_i^a	47.05	1.75	−7.23	−1.37		
	$\delta_i^a-\delta_i^e$	−4.75	−2.74	−4.43	0.39		
$OCOCH_3$	δ_i^e	45.79	5.03	−2.38	−1.73	CF_2Cl_2	40
	δ_i^a	42.08	2.76	−6.34	—		
	$\delta_i^a-\delta_i^e$	−3.71	−2.27	−6.72	—		
NO_2	δ_i^e	57.59	3.88	−2.78	−2.41	CS_2	42
	δ_i^a	54.02	1.10	−5.85	−1.26		
	$\delta_i^a-\delta_i^e$	−3.57	−2.78	−3.07	1.15		
NC	δ_i^e	24.86	6.67	−2.64	−1.82	CF_2Cl_2	40
	δ_i^a	23.29	3.52	−6.87	−1.82		
	$\delta_i^a-\delta_i^e$	−1.57	−3.15	−4.23	0.0		
CN	δ_i^e	1.38	2.81	−1.93	−1.93	CF_2Cl_2	40
	δ_i^a	0.09	−0.93	−4.53	−1.41		
	$\delta_i^a-\delta_i^e$	−1.29	−3.74	−2.60	0.52		
HgOAc	δ_i^e	20.30	—	—	—	$CDCl_3$	49
	δ_i^a	24.78	—	—	—		
	$\delta_i^a-\delta_i^e$	4.48	—	0.0	—		
CH_3	δ_i^e	5.96	9.03	0.05	−0.22	*	44
	δ_i^a	1.40	5.41	−6.37	−0.06	*	
	$\delta_i^a-\delta_i^e$	−4.56	−3.62	−6.42	0.16		
$Sn(CH_3)_3$	δ_i^e	−2.75	3.37	1.48	−0.57	CD_2Cl_2	84
	δ_i^a	—	—	−1.61	—		
	$\delta_i^a-\delta_i^e$	—	—	−3.09	—		
$Pb(CH_3)_3$	δ_i^e	8.54	6.16	2.56	−0.85	CD_2Cl_2	84
	δ_i^a	11.22	4.69	−1.62	−0.85		
	$\delta_i^a-\delta_i^e$	2 68	−1.47	−4.18	0.0		

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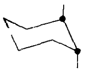
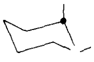
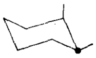
*Data obtained by optimising the additive scheme for the calculation of the chemical shifts for polysubstituted compounds.

In principle the inclusion of non-additive corrections may lead to an improvement of the agreement between the experimental and calculated chemical shifts. An improved scheme of increments has been proposed so far only for polymethylcyclohexanes[44] and it was possible to achieve agreement with experiment within the limits of several tens of p.p.m. As regards the increments $\Delta_i(X)$ themselves, the upfield shift of the signal of the γ-carbon atom in the axial conformer (on average by 5–6 p.p.m. relative to the equatorial conformer) is the most interesting feature. This shift (the so called γ-effect), first observed by Grant and Cheney[89] for methylcyclohexanes, is interpreted in the general case as reflecting the interaction "through space" of the hydrogen atoms attached to the γ-carbon atoms in the ring with the substituent.

Table 12. The non-additive corrections for the calculation of ^{13}C NMR chemical shifts for substituted carbon atoms in 1,2-derivatives of cyclohexane (in p.p.m.).

Conformation*	Substituents		
	CH_3, CH_3	Cl, Cl	Br, Br
	2.45[44]	4.7[42]	6.5[61]
	—	6.7[42]	9.2[61]
	3.43[44]	6.9[42]	—
	2.91[44]	6.9[42]	—

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*The atom considered is designated by a filled circle.

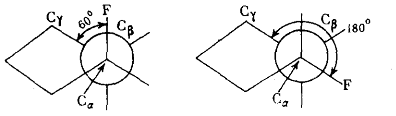
According to Grant and Cheney[90], the γ-effect depends on the distance r_{CH} and the angle θ which the C–H bond of the methyl group makes with the C...H line. The above dependence is described by the formula

$$\Delta\gamma = 1680 \cosh\,\theta \cdot \exp(-2.67 r_{CH}). \qquad (18)$$

The simplicity of this purely geometrical model explains why γ-effects have aroused interest in the literature on the conformational analysis of six-membered heterocycles[91,92]. It is noteworthy that in certain cases the γ-effect is weaker (for example, in the case of the F, OCH_3, and NO_2 substituents; see Table 11) and is altogether absent for mercury-substituted compounds[49]. The attempts at experimental determination of the dependence of $\Delta\gamma$ on r_{CH} (or r_{CX}) were unsuccessful (see, for example, the analysis of the γ-effects in fluorine-substituted steroids[93]).

By considering now the narrower class of halogenocyclohexanes, it is possible to trace the dependence of the chemical shifts on the electronegativity of the substituent (Fig. 4). With increase of Pauling's electronegativity E, the chemical shifts of the α-carbon atom increase, those of the β- and γ-atoms decrease, and for β-atoms the dependence is close to linearity. The corresponding differences $\Delta\delta = \delta_i^e - \delta_i^a$ are $\Delta\delta_\alpha = -7-5$, $\Delta\delta_\beta = 2.5-4.5$, $\Delta\delta_\gamma = 4-6$, and $\Delta\delta_\delta = 0--1$ (all the values are expressed in p.p.m.).

Comparatively little is known about the spin–spin coupling constants[44] involving ^{13}C nuclei (in substituted cyclohexanes); some results may be found in the papers of Subbotin and Sergeyev[39] and Weigert and Roberts[71]. A study of the low-temperature spectra of fluorocyclohexane showed all the $^{13}C-^{19}F$ spin–spin coupling constants for the interaction involving the carbon atoms in the individual conformers are different (these constants are listed in Tables 13). The $^3J(^{13}C-^{19}F)$ constant undergoes the most pronounced changes. The difference between the corresponding constants is probably due to the dependence of the constant $^3J(^{13}C-^{19}F)$ on the dihedral angle Φ between the $FC_\alpha C_\beta$ and $C_\alpha C_\beta C_\gamma$ planes. The dihedral angles are 60° and 180° for the axial and equatorial conformers respectively.



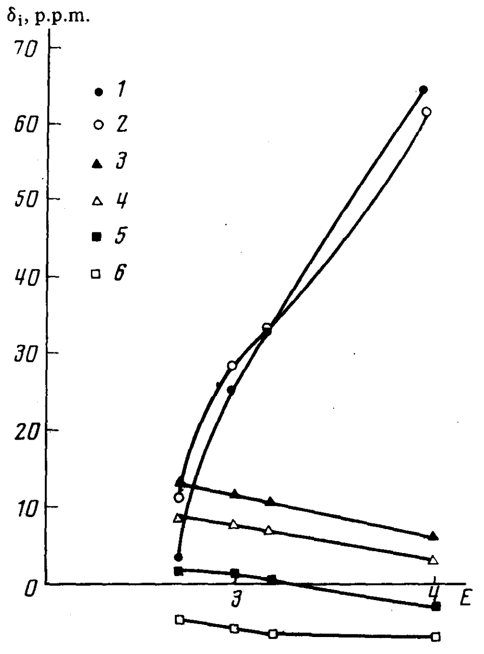


Figure 4. Dependence of the ^{13}C NMR chemical shift of the α-, β-, and γ-carbon atoms in the axial (a) and equatorial (e) conformers of halogenocyclohexanes on Pauling's electronegativity: 1) α_e; 2) α_a; 3) β_e; 4) β_a; 5) γ_e; 6) γ_a.

Assuming that the dependence of the constants $^3J(^{13}C-^{19}F)$ on the dihedral angle Φ is described by the "Karplus" curve corresponding to a function of the type $A + B\cos^2\Phi$, it is possible to estimate from the data in Table 13 the coefficients A and B, which yields $A = -2.5$ Hz and $B = 14$ Hz; thus the constant $^3J(^{13}C-^{19}F)$ probably changes sign in the vicinity of $\Phi = 0$. The absolute sign of the constant $^3J(^{13}C-^{19}F)$ is discussed by Hinton and Jaques[94].

There is at present no reliable information about the constants $J(^{13}C-H)$ for the compounds under consideration. The limited data obtained from ^{13}C NMR spectra of certain cyclic compounds[4,95] show that the constants $^1J(^{13}C-H)$ can be used in stereochemical studies, since a difference is observed between the constants for the axial and equatorial protons†.

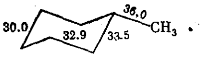
Table 13. The spin–spin coupling constants $J(^{13}C-^{19}F)$ (Hz) for fluorocyclohexane conformers at 183 K.[39]

SSC constant	Position of carbon atom			
	α	β	γ	δ
J_a,	167.0	21.5	1.0	<1
J_e,	172.2	17.7	11.5	2.0
$\lvert J_e - J_a \rvert$	5.2	3.8	10.5	~1

The constants $J(^{13}C-^{13}C)$ for coupling between carbon atoms linked by a σ bond may become yet another useful source of information. In recent years there has been a significant growth of interest in studies on these spin–spin coupling constants[97,98] in connection with advances in the technique of the recording of ^{13}C NMR spectra and in the calculation of spin–spin coupling constants. In particular, Gunther and Herrig[98] proposed on the basis of a compilation of experimental data an equation describing the dependence of $^1J(^{13}C-^{13}C)$ on the C–C bond length. If both carbon atoms are sp^3-hybridised, the equation becomes

$$J(^{13}C-^{13}C) = (-167.2 \pm 9.4)\,r_{CC} + (294.4 \pm 13.5). \qquad (19)$$

The constants $J(^{13}C-^{13}C)$ for the class of compounds under consideration have been reported so far only in the case of methylcyclohexane[42] (equatorial conformer). The $^{13}C-^{13}C$ constants for the corresponding C–C bonds are indicated below:



The similarity of the constants for the given compound shows that the C–C bond lengths differ very insignificantly (not more than by 0.02 Å).

oOo

Thus ^{13}C NMR spectroscopy has permitted definite progress in the solution of the classical problem of conformational analysis involving the study of equilibria between the conformers of substituted cyclohexanes. This progress consists in a significant expansion of the range of objects investigated, the discovery of universal methods for the measurement of equilibrium constants, and experimental study of ring inversion dynamics. In certain cases

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†The ^{13}C–H constants for cyclohexane itself have been obtained in a recent study[105] of the low-temperature ^{13}C NMR spectra of $[D_{11}]$cyclohexane: $^1J(^{13}C-H_a) = 122.44$; $^1J(^{13}C-H_e) = 126.44$; $^2J(^{13}C-H_a) = -3.94$; $^2J(^{13}C-H_e) = -3.69$; $^3J(^{13}C-H_a) = 2.12$; $^3J(^{13}C-H_e) = 8.12$; $^4J(^{13}C-H_a) = -0.31$; $^4J(^{13}C-H_e) = -0.50$ (all the values are expressed in Hz).

the accuracy of these methods, based on ^{13}C NMR spectra, is not inferior to that of other physical and chemical methods.

We may recall that ^{13}C NMR spectroscopy has been used recently to solve also other more complex problems of dynamic stereochemistry. In particular it has been possible to achieve with the aid of ^{13}C NMR a definite understanding of the conformational transformations in cyclo-octane[99], some of its derivatives[100,101], certain moderately large and large saturated rings[102], and cyclic ketones[103,104].

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Study of Short-lived Chlorine- and Sulphur-containing Radicals by the Spin-trapping Method

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The general aspects of the method for the identification and study of short-lived radicals in the liquid phase by EPR using spin-trapping agents are discussed and the available literature data for the application of the spin-trapping method to the study of short-lived chlorine- and sulphur-containing radicals and reactions involving them are surveyed. Certain methodological solutions, which make it possible to use the method in the study of complex radical reactions, are examined.

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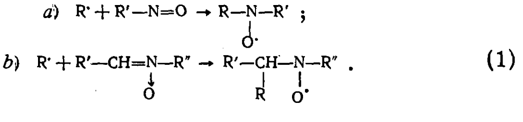
I. INTRODUCTION

Many free radicals are extremely unstable paramagnetic species and their identification by EPR is possible only when their steady-state concentration is sufficiently high. The existing methods for the direct investigation of short-lived radicals in the liquid phase by EPR therefore consist either in a constant maintenance of a fairly high concentration of the radicals in the spectrometer resonator (flow method[1,2]) or in an increase of the lifetime of the radicals by reducing the temperature[3,4]. These methods suffer from the following disadvantages. In the first case considerable amounts of starting materials are required, and in the second account must be taken of the fact that radical processes can take place in different ways depending on the temperature, so that the results obtained, for example, at −100°C, do not always agree with the reaction mechanism at room or higher temperatures[5,6]. Furthermore, the above methods are very complex experimentally.

Towards the end of the 1960s, a new method was developed for the investigation of the EPR of short-lived radicals in the liquid phase called the "nitroxide method"[7] or the "spin-trapping method"[8]. The essential feature of this method is that the short-lived radicals R˙ formed during the homolytic reaction add to a "spin-trapping agent" (a nitroso-compound, a nitrone, or another suitable radical acceptor) specially introduced into the reaction mixture, which leads to the formation of nitroxy-radicals ("spin-adducts"[8]), for example:



$$a)\quad R^{\cdot}+R'{-}N{=}O \rightarrow R{-}\underset{\substack{|\\ O^{\cdot}}}{N}{-}R'\ ;$$

$$b)\quad R^{\cdot}+R'{-}CH{=}\underset{\substack{\downarrow\\ O}}{N}{-}R'' \rightarrow R'{-}\underset{\substack{|\\ R}}{CH}{-}\underset{\substack{|\\ O^{\cdot}}}{N}{-}R''\ . \qquad (1)$$

The nitroxy-radicals formed are in many cases sufficiently stable for investigation by EPR. The EPR spectrum of the spin-adduct makes it possible to arrive at a conclusion concerning the structure of the radical R˙ detected†.

This method naturally suffers from the usual disadvantages of an indirect procedure compared with direct procedures. Nevertheless it has many advantages which have ensured its extensive development and application‡. The largest of spin labels available makes it virtually universal for the detection of a wide variety of radicals. The method is extremely simple experimentally and does not require large amounts of starting materials.

Several reviews devoted to studies on a wide range of different radicals by this method were published in 1970–71.[7,8,14]. However, during this initial period of the development of the method, studies were performed mainly on model reactions, i.e. those where known radicals were generated, and the possibility of their detection by particular trapping agents and the relation between the EPR parameters and the structure of the "trapped" radical were investigated, new trapping agents were proposed, etc. The results served as the basis for the

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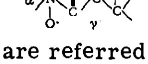
†The following nomenclature is used to designate the positions in nitroxy-radicals[9]:



(the RR′NO˙ radicals are referred to in the literature as "nitroxide" and "nitroxy-radicals"[10]. Rozantsev[11,12] argues convincingly that the term "nitroxy-radical" is more justified and this is the term which we shall use in the present review).

‡The method became rapidly popular and, as early as 1971, a paper was published[13] warning investigators against being unduly attracted by this procedure and indicating the limits of its applicability.

employment of the spin-trapping method for the investigation of certain fairly complex radical processes.

Many new investigations devoted to both the development of the method and to its employment in the study of radicals and mechanisms of radical reactions, have now accumulated in the literature. In this review we shall deal mainly with the application of the spin-trapping method to the study of chlorine- and sulphur-containing radicals and the reactions involving them.

II. GENERAL PROBLEMS OF THE SPIN-TRAPPING METHOD

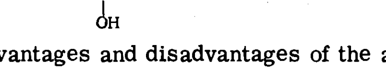
The nitroxy-radicals formed as a result of the addition of short-lived radicals to the trapping agent are characterised primarily by a triplet signal in the EPR spectrum due to the interaction of the unpaired electron with the ^{14}N nucleus. The *g*-factors for different nitroxy-radicals are very similar[7], but, depending on the substituents at the nitrogen atom, the hyperfine interaction constant a_N for different nitroxy-radicals varies within fairly broad limits—from 4–5 G for diacylnitroxy-radicals[15] to 25 to 28 G for alkoxyalkylnitroxy-radicals[16]. Even the values of a_N for different spin-adducts can therefore yield, to a first approximation, information about the nature of the short-lived radical detected by the trapping-agent. Furthermore, if nuclei with non-zero spins are present in the α- and β-positions relative to the nitroxy-group, then the EPR spectrum shows an additional splitting of the lines of the main triplet. Thus the hyperfine structure (HFS) of the spectrum and the hyperfine interaction (HFI) constants provide in this case additional and very important information for the identification of the "trapped" radical. Lines for hyperfine interaction with more remote nuclei are resolved only in exceptional individual instances; as a rule, hyperfine interactions are manifested only by a smaller or greater broadening of the lines of the main triplet.

It is noteworthy that the spin-trapping method is very convenient and effective for demonstrating the radical mechanism of a particular reaction and for the qualitative identification of the radicals formed. The method has been used recently also to investigate reactions proceeding via a one-electron transfer mechanism (see, for example, Refs. 17–19). As regards the determination of quantitative data, for example, the relative concentration of the radicals formed, then in the general case this cannot be done on the basis of a comparison of the integrated intensities of the spectra of their spin-adducts. This is because not all the radicals are trapped to an equal extent and not all the spin-adducts are equally stable. Quantitative estimates therefore require the knowledge of the relative rates of reaction with the given trapping agent of the radicals being compared and of the rates of the subsequent transformations of the nitroxy-radicals formed. It is therefore of interest to note the studies published recently on the quantitative determination by the spin-trapping method of the yields of radicals formed in the radiolysis of methanol under various conditions[20,21].

1. Spin-Trapping Agents

The range of compounds used as spin-trapping agents is now fairly wide. As already mentioned, nitroso-compounds and nitrones are mainly used for this purpose.

a) Nitroso-compounds. Tertiary or aromatic nitroso-compounds are as a rule used as trapping agents, so that the EPR spectrum of the spin-adduct formed is not complicated by the hyperfine interaction with the β-hydrogen atoms of the nitroso-compound. Among non-aromatic nitroso-compounds, 2-methyl-2-nitrosopropane (nitroso-t-butane, MNP) and its deuterated analogue[14], as well as 2-methyl-2-nitroso-3-butanone (MNB)[7] are most frequently used. 2-Nitroso-2-trifluoromethylhexafluoropropane[22] and trisethoxycarbonylnitrosomethane[23] have been proposed recently. A number of workers put forward a very interesting combination in a single compound of sources of the spin-trapping agent and of the radicals[24-29]. They showed that, when aryl-*N*-hydroxytriazenes are oxidised by lead dioxide, aryl radicals and a nitroso-compound, capable of behaving as a spin-trapping agent, are formed simultaneously:



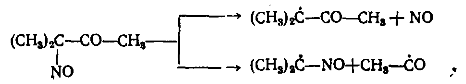
$$\underset{\displaystyle\ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ OH}{Ar{-}N{=}N{-}N{-}R} \xrightarrow{PbO_2} Ar^{\cdot} + N_2 + R{-}N{=}O \quad . \tag{2}$$

The advantages and disadvantages of the above trapping agents are widely discussed in the literature; MNP is the most universal agent. It will be clear from subsequent exposition (see Sections III–V) that the majority of radicals react with MNP to form fairly stable and readily identifiable spin-adducts. However, this compound suffers also from many disadvantages. Firstly, it is dimeric in the solid state, and is converted into the active monomeric form in solution to only a slight extent; complete transformation into the monomeric form is achieved under the influence of radiation[30]. Secondly, when acted upon by lead dioxide or ultraviolet light, or on heating[8], MNP may decompose·

$$\begin{gathered}(CH_3)_3C{-}N{=}O \rightarrow (CH_3)_3\dot{C} + NO,\\ (CH_3)_3\dot{C} + (CH_3)_3C{-}N{=}O \rightarrow [(CH_3)_3C]_2N{-}\dot{O},\end{gathered} \tag{3}$$

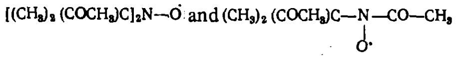
and the resulting t-butyl radicals may add to the initial molecule to form a nitroxy-radical, the spectrum of which consists of a triplet with $a_N = 15–17$ G (depending on the solvent used)[16]. This triplet is frequently so intense that it may overlap the lines corresponding to the other spin-adducts formed§. In addition, when MNP is used, the reaction mixture often has to be freed from oxygen to avoid the formation of certain secondary radicals[32].

MNB is also present as an inactive dimer, which partly dissociates in solution to the monomer[7]. Ultraviolet irradiation promotes such dissociation, causing at the same time the fragmentation of the nitroso-compound into radicals:



$$(CH_3)_2\underset{\displaystyle NO}{\underset{|}{C}}{-}CO{-}CH_3 \longrightarrow \begin{cases} (CH_3)_2\dot{C}{-}CO{-}CH_3 + NO \\ (CH_3)_2\dot{C}{-}NO + CH_3{-}\dot{C}O \end{cases} \tag{4}$$

These add to the initial molecule to form the spin-adducts



$$[(CH_3)_2(COCH_3)C]_2N{-}\dot{O} \text{ and } (CH_3)_2(COCH_3)C{-}\underset{\displaystyle O^{\cdot}}{\underset{|}{N}}{-}CO{-}CH_3$$

characterised in the ESR spectrum by triplets with $a_N = 14$ to 15 G[16] and 7–8 G[7] respectively.

A distinctive feature of this trapping agent is that radicals containing chlorine atoms at the radical centre cannot be detected with its aid[33]. This limits its applicability, on

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§Since the main absorption band of MNP is in the region of 680 nm, its fragmentation may be avoided by using shorter-wavelength radiation[31].

the one hand, and constitutes a significant advantage in the selective detection of various radicals in complex homolytic reactions, on the other (see Section V).

2-Nitroso-2-trifluoromethylhexafluoropropane (nitrosoperfluoro-t-butane, NFB) is an extremely convenient trapping agent for chlorine-containing radicals. For example, its spin-adduct with $Cl_3C^{\cdot}$ has an EPR spectrum which can be more readily interpreted than that of the corresponding MNP adduct (see Section III). A disadvantage of NFB is, as for the other nitroso-compounds mentioned above, its decomposition under the influence of radiation. The nitroxy-radical formed as a result of a secondary reaction,

$$(CF_3)_3C{-}N{=}O \rightarrow [(CF_3)_3\dot{C} + NO\ ,$$

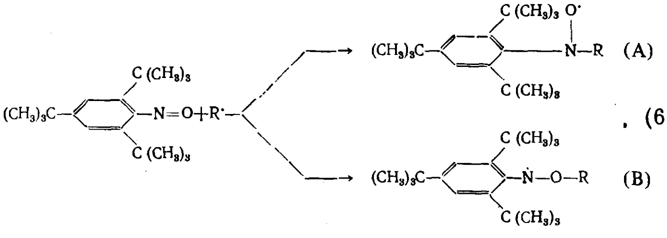
$$(CF_3)_3\dot{C} + (CF_3)_3C{-}NO \rightarrow [(CF_3)_3C]_2N{-}\dot{O}\ , \qquad (5)$$

gives rise to a triplet with a_N = 11.9 G in the spectrum, with very appreciably broadened (~6 G) lines owing to hyperfine interaction with γ-fluorine atoms[34].

The application of trisethoxycarbonylnitrosomethane is so far restricted to isolated examples only[23]. It is apparently convenient for the detection of alkyl radicals. There are as yet no literature data for investigations of chlorine- and sulphur-containing radicals with its aid.

Among aromatic nitroso-compounds, only nitrosobenzene was used in the early stages[8]. However, although this trapping is fairly universal, it suffers from a significant disadvantage: the EPR spectrum of the corresponding spin-adducts consists of many components owing to hyperfine interaction with the *o*- and *p*-hydrogen atoms in the benzene ring (the splitting by the *m*-hydrogen atoms is as a rule insignificant—less than 1 G). This hinders to a large extent the identification of the "trapped" radical.

Nitrosodurene[35] and 2,4,6-tri-(t-butyl)nitrosobenzene, proposed subsequently[36,37], are much more convenient in this respect. The latter trapping agent is of interest also because, depending on the nature of the radical combining with it, different spin-adducts are formed:

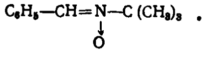


. (6)

Primary alkyl radicals as well as phenyl and phenylthio-radicals give rise to the nitroxy-radical A, while tertiary radicals form the anilino-radical B; secondary radicals form a mixture of the two products. The spin adducts A and B can be readily distinguished on the basis of their ESR spectra (the *g*-factors for A and B are respectively 2.006–2.007 and 2.0035–2.0040).[36]

An advantage of this trapping agent is that it is monomeric also in the solid state and, furthermore, even if it does decompose under the influence of ultraviolet radiation[38], it never gives any additional EPR signals under these conditions. It is apparently unsuitable for the identification of radicals of the type $\dot{C}Cl_3$ and $\dot{C}HCl_2$.[36]

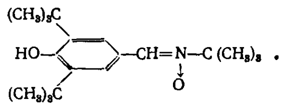
(b) Nitrones. Among nitrones, *N*-t-butyl α-phenyl nitrone (BPN) is most frequently used as a spin-trapping agent[8].



$$C_6H_5{-}CH{=}\underset{\downarrow \atop O}{N}{-}C(CH_3)_3\ .$$

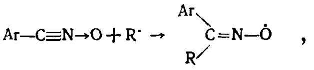
In addition, the use of *N*-t-butyl nitrone[39], α-*N*-diphenyl nitrone[40] and cyclic nitrones[8,41] has been described. The advantages and disadvantages of nitrones have been analysed in detail in a review[8]. We shall mention only that, in contrast to nitroso-compounds, nitrones make it possible to detect chlorine (see Section III) and hydrogen atoms[8,20]. However, they suffer from the important disadvantage that the spectrum of the spin-adducts formed as a result of the addition of short-lived radicals (see Scheme 1, b) has a hyperfine structure due solely to the splitting of the lines by the interaction with the nitrogen and β-hydrogen atom (a triplet of doublets). For the majority of spin-adducts, a_N and $a_{H-\beta}$ depend little on the structure of the trapped radical. An unambiguous identification of the radicals is therefore often possible only on the basis of the comparison of the resulting EPR spectrum with that of the corresponding spin-adduct, obtained by a standard procedure[8]¶.

A very interesting "bifunctional" trapping agent has been proposed[42]:



Alkyl and aryl radicals add to it with formation of nitroxy-radicals, while alkoxy-radicals abstract the hydroxyl-hydrogen, giving rise to a stable phenoxy-radical.

(c) Other trapping agents. Aromatic nitrile oxides, forming very stable spin-adducts (iminoxy-radicals) with short-lived radicals



$$Ar{-}C{\equiv}N{\rightarrow}O + R^{\cdot} \rightarrow \begin{matrix} Ar \\ R \end{matrix}\!\!>\!C{=}N{-}\dot{O}\ , \qquad (7)$$

are extremely convenient trapping agents for hydrocarbon radicals[43]. However, they are relatively unsuitable for chlorine-containing radicals, because of an unduly low value of a_{Cl} (for example, a_{Cl} = 0.5G for $Ar{-}\underset{CCl_3}{\underset{|}{C}}{=}N{-}\dot{O}$).

The above data permit the conclusion that complex radical reactions should evidently be investigated with the aid of various trapping agents, taking into account their advantages and disadvantages, selectivity, etc, and not just a single trapping agent.

2. Experimental Conditions

Most of the reactions described in the literature were investigated directly in the resonator of the EPR spectrometer. A small amount of the trapping compound is usually added to the experimental reaction mixture and the sealed tubes containing the solution are placed in the resonator where they are irradiated, heated, or cooled (depending on the conditions required for the reaction). As a rule, the reaction mixture is not freed from oxygen. However, it has been shown (see, for example, Zubarev et al.[20]), that the presence of oxygen reduces the intensity of the spectral

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¶The use of N-t-butyl α-(2,4,6-trimethoxyphenyl) nitrone, the spin-adducts of which are characterised by a much greater sensitivity of $a_{H-\beta}$ to the nature of the trapped radical than for the spin-adducts of other nitrones, has been described recently[89].

signals and broadens individual lines. When necessary, oxygen is removed by evacuation or by passing a stream of an inert gas through the reaction mixture in the course of 10–15 min. Depending on the polarity of the reaction mixture, cylindrical or planar tubes are used[36].

The concentration of the trapping compound is as a rule 0.001–0.05 M for nitroso-compounds and 0.05–0.06 M for nirtones. Evidently the above concentrations are extremely approximate, since the choice of the concentration of the trapping agent for each given chemical reaction depends on a number of factors. Indeed, in the general case, apart from interaction with the molecules of the trapping agent, the test radicals are involved in other competing reactions with the molecules of the medium M:

$$\text{Initiator} \rightarrow \dot{R}_1 \quad , \tag{8}$$

$$\dot{R}_1 + M \xrightarrow{k_1} \dot{R}_2 \quad , \tag{9}$$

$$\dot{R}_1 + RNO \underset{k_{-2}}{\overset{k_2}{\rightleftarrows}} R_1RN{-}\dot{O} \quad , \tag{10}$$

$$\dot{R}_2 + RNO \underset{k_{-3}}{\overset{k_3}{\rightleftarrows}} R_2RN{-}\dot{O} \quad . \tag{11}$$

The formation of spin-adducts at an adequate concentration requires that the conditions $k_2 \gg k_{-2}$ and $k_2 \gg k_{-3}$ be fulfilled. It follows even from this simple scheme that the ratio of the concentrations of the nitroxy-radicals $R_1RN\dot{O}$ and $R_2RN\dot{O}$ in solution in the steady state depends on the concentration of the trapping agent, the substance M, and the rate constants k_1 and k_2. Thus, without knowing the constants (the constants k_2 are known only in a few instances[44–46]), it is impossible to determine beforehand the required concentration of the trapping compound.

(a) Solvents. The choice of solvent has been discussed in detail[7]. The most convenient solvent above 5°C is apparently benzene, since, in contrast to many other solvents employed, it does not form radicals under the experimental conditions†. Methylene chloride is frequently used at low temperatures[7], but one should note that, following ultraviolet irradiation in the presence of MNP, signals due to the nitroxy-radical $H{-}CO{-}\underset{\dot{O}}{\underset{|}{N}}{-}C(CH_3)_3$ formed via a side reaction, consisting of a triplet of doublets with $a_N = 7.0$ and $a_H = 1.41$ G are usually observed in this case[47].

(b) Temperature. The reactions are as a rule carried out at room temperature, but the stability of many nitroxy-radicals depends significantly on temperature. Furthermore, as already mentioned, the reaction may lead to different radicals, depending on temperature. Therefore, in the study of radical processes by the spin-trapping method, the temperature plays an extremely important role (see Section V). It is noteworthy that the parameters of the EPR spectra of nitroxy-radicals are almost independent of temperature.

(c) Methods of generating radicals. This problem has been discussed in fair detail in a number of studies[7,8,14,48]. Here it is of interest to note certain differences between the photochemical methods for the generation of radicals which are investigated directly and radicals identified in the form of their spin-adducts. Owing to the very short lifetime of the radicals, ultrahigh-pressure 1–2 kW mercury lamps are used to obtain them in sufficient concentrations when a flow method[2] is used and in low-temperature experiments[4]. In the study of radicals by the spin-trapping method it is sufficient to employ 100–150 W mercury lamps. It is desirable that the arrangement for ultraviolet irradiation should include appropriate filters, gratings, and diaphragms for regulating the wavelength and intensity of the incident light. Since certain nitroxy-radicals are fairly stable above room temperature, many of them can be obtained by thermal as well as photochemical methods[47].

Numerous chlorine-containing radicals have been obtained by abstracting hydrogen from the correspoding chloroalkanes by the phenyl radicals formed in the oxidation of hydroxytriazenes (Scheme 2).[28] Thiyl radicals are as a rule generated by ultraviolet and γ-irradiation of the corresponding disulphides and thiols. In addition, they can be generated by abstracting hydrogen from thiols by various radicals obtained thermally or photochemically. Sulphonyl radicals are obtained from the corresponding sulphonyl halide as a result of the abstraction of the halogen by triethylsilyl radicals or photochemically (see Section IV).

III. EPR SPECTRA OF NITROXY-RADICALS—SPIN-ADDUCTS OF CHLORINE-CONTAINING RADICALS

Chlorine-containing nitroxy-radicals with one, two, and three chlorine atoms in the β-position, i.e. $R_nCCl_{3-n}N(\dot{O}){-}R'$, are in many cases sufficiently stable to be investigated by EPR under steady-state conditions. This applies particularly to spin-adducts of chlorine-containing radicals with MNP and its perdeutero- and perfluoro-derivatives as well as nitrosodurene.

The hyperfine structure of the spectra of chlorine-containing nitroxy-radicals is extremely complex. This is caused, firstly, by the fact that the chlorine nucleus has a spin of 3/2, which leads to $2n \times 3/2 + 1$ (n is the number of equivalent β-chlorine atoms) lines in the spectrum and, secondly, it arises because the two chlorine isotopes present in natural chlorine in fairly large amounts (75.53% of ^{35}Cl and 24.47% of ^{37}Cl) have different magnetic moments, (0.821 and 0.683 μ_B respectively) which leads to an increase of the multiplicity of the spectral lines as a result of the interaction of the unpaired electron with these nuclei.

This Section describes studies carried out on model examples of known chlorine-containing radicals in order to develop further the spin trapping method as well as studies in which the method has been used to investigate complex chemical processes involving the intermediate formation of short-lived chlorine-containing radicals.

Chlorine-containing radicals can be arbitrarily divided into three groups: (1) chlorine atoms; (2) mono- and poly-chloromethyl radicals; (3) higher chlorine-containing radicals.

1. Chlorine

The spin-adducts of chlorine of the type $Cl{-}N(\dot{O}){-}R$ are unknown. The attempt to add chlorine to MNP[8] has been unsuccessful, which indicated, according to the

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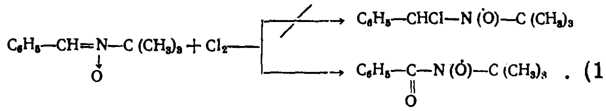
†Certain aryl radicals can add to benzene with formation of the corresponding substituted cyclohexadienyl radicals, which are then detected by the trapping agent[90,91].

author[8], the instability of the expected spin-adduct. The preparation of the nitroxy-radicals $R^1R^2CCl-N(\dot{O})R$, formed both by the interaction of chlorine donors with nitrones[8,49-52] and by the addition of the radical $R^1R^2\dot{C}Cl$ to nitroso-compounds, has been described. The first method of obtaining β-chloronitroxy-radicals is discussed below.

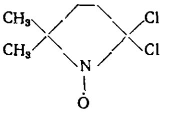
The interaction of chlorine with α-phenyl-t-butylnitrone (PBN) in benzene at room temperature leads to the benzoyl-t-butylnitroxy-radical and not to the spin-adduct—t-butyl-α-chlorobenzylnitroxy-radical[53]:



$$C_6H_5-CH{=}\underset{\downarrow\atop O}{N}-C(CH_3)_3 + Cl_2 \to \begin{cases} \not\to C_6H_5-CHCl-N(\dot{O})-C(CH_3)_3 \\ \to C_6H_5-\underset{\|\atop O}{C}-N(\dot{O})-C(CH_3)_3 \end{cases} \quad (12)$$

The same nitroxy-radical is formed in the reaction of PN with nitrosyl chloride[53], *N*-chlorosuccinimide[39], and poly-nitro-compounds[54].

Table 1. Parameters of the EPR spectra of $R-N(\dot{O})-R'$ nitroxy-radicals (chlorine spin-adduct).

No.	Trapping agent	R	R′	a_N, G	a_{Cl}, G	a_H, G	Method of synthesis of nitroxy-radicals	Temp. °C	Solvent	References
1	BPN	C_6H_5CHCl	$C(CH_3)_3$	12.1	6.05; 4.88*	0.75	$BPN + (CH_3)_3COCl$	35	C_6H_6	8,49
2	BPN	C_6H_5CHCl	$C(CH_3)_3$	12.1	6.0; 4 9*	0.8	$BPN + SO_2Cl_2 + h\nu$	20	C_6H_6	51
3	BPN	$C_6H_5CCl_2$	$C(CH_3)_3$	13.2	3.3	—	$BPN + (CH_3)_3COCl$	35	CCl_4	49
4	DMPO			10.67	3.57	—	$DMPO + Cl_2$ or $DMPO + (CH_3)_3COCl$	—	C_6H_6	50

*The values of a_{Cl} for ^{35}Cl and ^{37}Cl respectively.

Figure 1. The EPR spectrum of the t-butyl-α-chlorobenzylnitroxy-radical in benzene[49].

Subsequently it was possible to obtain t-butyl-α-chlorobenzylnitroxy-radicals by the interaction of PBN with t-butyl hypochlorite in the absence of oxygen[49] (Table 1, No. 1). The resulting EPR spectrum is illustrated in Fig.1. The doublet with a small splitting (a_H = 0.75 G) refers to the β-hydrogen atom. The overlapping quartets result from the hyperfine interaction with the ^{35}Cl and ^{37}Cl nuclei. It is clear from the spectrum that the larger splitting constant corresponds to $a_{^{35}Cl}$ = 6.05 G and the smaller constant corresponds to $a_{^{37}Cl}$ = 4.88 G.

The same spectrum has been obtained following the interaction of PBN with trichlorosilane and chlorotrimethylsilane[49]. The authors suggest that in this case the reaction proceeds with the intermediate formation of t-butyl hypochlorite. The mechanism of the formation of monochloronitroxy-radicals has not been investigated by this procedure[49]. t-Butyl-monochlorobenzylnitroxy-radicals have been obtained also in the photolysis of sulphuryl chloride in the presence of PBN[51,52] (Table 1, No. 2). The authors believe that in this case a chlorine atom adds to PBN.

On the basis of the EPR spectrum in CCl_4 of the product obtained by treating PBN with t-butyl hypochlorite in a gaseous phase[49] (Table 1, No. 3), the authors attributed the structure $C_6H_5CCl_2-N(\dot{O})C(CH_3)_3$ to the nitroxy-radical obtained.

The EPR spectra of the spin-adducts of various radicals with the cyclic nitrone 5,5-dimethyl-1-pyrrolin-1-oxyl (DMPO) have been obtained[50]. According to the results, chlorine as well as t-butyl hypochlorite react with DMPO to form a dichloro-derivative (Table 1, No. 4).

It is seen from the foregoing that at least some of the nitroxy-radicals investigated are products of more complex processes than the direct addition of chlorine to the trapping agent. This is particularly clear from the last two examples, since substitution of β-hydrogen by chlorine also occurs in these reactions.

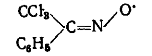
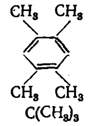
2. Mono- and Poly-Chloromethyl Radicals

(a) The trichloromethyl radical. The trichloromethyl radical has been widely investigated because of its considerable role in synthetic organic chemistry[55-57] and because it is readily obtained when CCl_4, $CHCl_3$, and CCl_3Br are acted upon by radical-forming agents as well as in the photolysis of CCl_3Br.

The study of the spin-adducts of the radicals $CCl_3^{\bullet}$ with nitroso-compounds initially involved many difficulties. When $CCl_3^{\bullet}$ radicals are generated by the irradiation of $CHCl_3$ or CCl_4 with ultraviolet light in the presence of benzoyl peroxide and various nitroso-compounds, the more stable chlorocarbonyl nitroxy-radicals $Cl-CO-N(\dot{O})-R$ are formed together with the trichloromethylnitroxy-radicals $\dot{C}Cl_3-N(O)-R$, which led to confusion in the determination of the parameters of the spectra of trichloromethylnitroxy-radicals (for a more detailed discussion, see below). On the other hand, the first correctly identified nitroxy-radical of this type, namely $(CCl_3)_2N\dot{O}$, was detected[58] in the synthesis of trichloronitrosomethane and not in a mixture known to contain $\dot{C}Cl_3$ radicals[58]. The constants a_N = 11.8 G and a_{Cl} = 1.25 G were determined in this investigation[58] which constituted the first example of the determination of the hyperfine coupling constants for β-chlorine atoms in nitroxy-radicals (Table 2, No. 1). These data were subsequently confirmed[48].

The spectrum of the nitroxy-radical $CCl_3-N(\dot{O})-C(CH_3)_3$ was described for the first time by Leaver et al.[31] It was characterised by the following parameters: a_N = 12.73; a_{Cl} = 2.41 G; g = 2.0065 (Table 2, No. 5). This spectrum was obtained on irradiation (λ ≃ 300 nm) of a solution of indole or its methyl derivatives in solution in CCl_4 containing MNP. The same workers stated[59] that this spectrum can be obtained by abstracting hydrogen from $CHCl_3$ in the presence of MNP. When a spectrum with a resolved hyperfine structure, due to the interaction with the four

Table 2. Parameters of the EPR spectra of $R-N(\dot{O})-R'$ nitroxy-radicals (spin-adducts of mono- and poly-chloromethyl radicals).

No.	Trapping agent	R	R′	a_N, G	a_{Cl}, G	Method of generation of radicals	Temp., °C	Solvent	Refs.
1	CCl_3NO	CCl_3	CCl_3	11.8	1.25	decomposition of CCl_3NO	room	—	48, 58
2	$(CH_3)_3CNO$	CCl_3	$C(CH_3)_3$	12.5	2.2	$CHCl_3$ + TBP***** + $h\nu$	—	—	61
3	$(CH_3)_3CNO$	CCl_3	$C(CH_3)_3$	12.4	2.3	$CCl_3Br + h\nu$	35	—	49
4*	$(CH_3)_3CNO$	CCl_3	$C(CH_3)_3$	12.73	2.41	CCl_4 + indole + $h\nu$	—	CCl_4	31, 59
5	$(CH_3)_3CNO$	CCl_3	$C(CH_3)_3$	12.2	2.2	$CCl_4 + (C_2H_5)_3SiH$ + TBP	—	CCl_4	66
		CCl_3	$C(CH_3)_3$	12.2	2.2	$CHCl_3$ + TBP + $h\nu$	—	$CHCl_3$	66
6	$(CH_3)_3CNO$	CCl_3	$C(CH_3)_3$	12.9	2.2	$CHCl_3 + C_6H_5-N{=}N-N(OH)-C(CH_3)_3 + PbO_2$	room	$CHCl_3$	28
7	$(CD_3)_3CNO$	CCl_3	$C(CD_3)_3$	12.5	2.2	$CHCl_3$ + TBP + $h\nu$	30	$CHCl_3$	47
8	$(CF_3)_3CNO$	CCl_3	$C(CF_3)_3$	13.1	1.5	$CCl_4 + (C_2H_5)_3SiH$ + TBP or $CHCl_3 + h\nu$	—	CCl_4, $CHCl_3$	22
9**	$C_6H_5-C{\equiv}N{\to}O$			32.7	0.5	$CHCl_3$ + TBP + $h\nu$	room	$CHCl_3$	43
10	Nitroso-durene	CCl_3		10.73	1.31	$CCl_4 + [(C_6H_5)_3Sn]_2 + h\nu$	room	CCl_4	35
						$CHCl_3$ + TBP + $h\nu$	room	$CHCl_3$	35
11	$(CH_3)_3CNO$	$CHCl_2$	$C(CH_3)_3$	12.2	3.27; 2.7******	$CH_2Cl_2 + C_6H_5N{=}N-N(OH)-C(CH_3) + PbO_2$	room	CH_2Cl_2	28
12	$(CD_3)_3CNO$	$CHCl_2$	$C(CD_3)_3$	11.7	4.8; 4.05******	CH_2Cl_2 + di-t-butyl peroxydioxalate	30	CH_2Cl_2	47
13***	$(CF_3)_3CNO$	$CHCl_2$	$(CF_3)_3C$	14.0	1.6	CH_2Cl_2 + TBP + $h\nu$	25	CH_2Cl_2	22, 66
i4****	$(CH_3)_3CNO$	CH_2Cl	$C(CH_3)_3$	11.9	8.35; 6.90******	$CH_2ClI + C_6H_5N{=}N-N(OH)-C(CH_3)_3 + PbO_2$	room	CH_2ClI	28

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*$g = 2.0065$.

**$g = 2.0048$.

***$a_H < 0.1$ G.

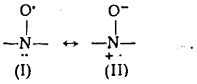
****$a_H = 3.55$ G.

*****t-butyl peroxide.

******the values of a_{Cl} for ^{35}Cl and ^{37}Cl respectively.

possible combinations of the nuclei of chlorine isotopes in the CCl_3 group, is obtained, each line of the main triplet of the ^{14}N signal should be split into 72 lines, of which only 10 were observed. The authors calculated the spectrum by an iterative procedure using the method of least squares; they took into account only the two most important isotope combinations: $^{35}Cl_3$ and $^{35}Cl_2{}^{37}Cl$. The best agreement with the experimental spectrum was obtained for $a_{^{35}Cl}$ = 2.46 G and $a_{^{37}Cl}$ = 2.05 G. Subsequently, the formation of the spin-adducts of the trichloromethyl radical with MNP was noted repeatedly (Table 2, Nos. 2-6).

It has been noted[49] that a_{Cl} for the bistrichloromethylnitroxy-radical is appreciably less than for the t-butyltrichloromethylnitroxy-radical (1.25 and 2.3 G respectively). The authors point out that this may be associated with the lower spin density at the nitrogen atom in the bistrichloromethylnitroxy-radical. The more pronounced electron-accepting properties of the CCl_3 group compared with the $(CH_3)_3C$ group favour structure (I) rather than structure (II):



$$\overset{O^{\cdot}}{\underset{\cdot\cdot}{-N-}} \leftrightarrow \overset{O^{-}}{\underset{+\cdot}{-N-}}$$

(I) (II)

(see also Refs. 14 and 60). The constants a_N differ less than the constant a_{Cl}. The authors[49] also do not rule out the possibility that the small difference between the planarities of the nitroxy-group, caused by the differences between the steric interactions in the above radicals, may likewise give rise to differences between the hyperfine coupling constants a_N and a_{Cl}.

The splitting of the ^{14}N signal due to the commonest combinations of chlorine isotopes (present in the mixture) in the CCl_3 group, i.e. $^{35}Cl_3$ and $^{35}Cl_2{}^{37}Cl$, was achieved for the first time by Perkins et al.[61] The EPR spectrum obtained when $CHCl_3$ was acted upon by TBP in the presence of MNP (Table 2, No. 2) consisted of three ten-component groups of lines, which partly overlapped (Fig. 2). It is seen from the insert in the figure that the extreme line is split into two components, which can be accounted for by the presence of different chlorine isotope combinations.

It has been shown[28] that the oxidation of 3-t-butoxy-1-phenyltriazene by lead dioxide (Scheme 2) in chloroalkanes leads to the formation of chlorine-containing radicals, which interact with the MNP formed simultaneously. The EPR spectrum then shows signals due to the corresponding spin-adducts. In particular, when the reaction was carried out in $CHCl_3$ or CCl_4, the product was the nitroxy-radical $CCl_3-N(\dot{O})-C(CH_3)_3$, whose spectrum was identical with that described by Perkins et al.[61] (Table 2, No. 6).

When a solution of TBP in chloroform containing benzonitrile *N*-oxide or *p*-chlorobenzonitrile *N*-oxide as the spin-trapping agent was irradiated with ultraviolet light (see Scheme 7), a spectrum with a_N = 32.7 G, a_{Cl} = 0.5 G, and g = 2.0048, corresponding to an iminoxy-radical with the CCl_3 group in the *syn*-position relative to the N-O bond, i.e.  , was obtained (Table 2, No. 9).[43] The formation of an iminoxy-radical by the oxidation of chloroaldoxime has also been described[62].

The values of a_N for the spectrum obtained in the detection of the trichloromethyl radical with the aid of 2-nitroso-2-trifluoromethylhexafluoropropane are greater and those of a_{Cl} are smaller (Table 2, No. 8) than for the corresponding spin-adduct obtained when the $CCl_3^{\bullet}$ radical adds to MNP; the spectrum of the spin-adduct with the fluorinated trapping agent is therefore better resolved (Fig. 3)[22].

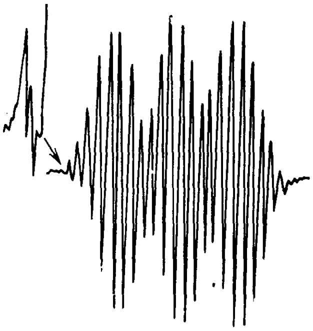


Figure 2. The EPR spectrum of the $CCl_3-N(\dot{O})-C(CH_3)_3$ radical. The insert on the left represents the splitting of the extreme line due to the presence of $^{35}Cl_3$ and $^{35}Cl_2{}^{37}Cl$.[61]

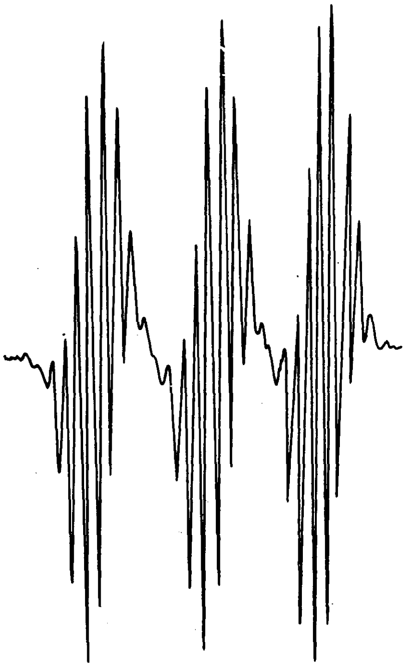
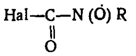


Figure 3. The EPR spectrum of $(CF_3)_3C-N(\dot{O})-CCl_3$.[66]

The trichloromethyl radical has also been detected with the aid of nitrosodurene when a solution of TBP in chloroform was irradiated and also when chlorine was abstracted from CCl_4 by triethylsilyl radicals[35] (Table 2, No. 10).

(b) The Hal−CO−N($\dot{O}$)−R nitroxy-radicals. Nitroxy-radicals of the type



$$Hal-\underset{\underset{O}{\|}}{C}-N(\dot{O})R$$

(III)

are some of the most important radicals of this kind, obtained by a side reaction during the formation of the spin-adducts of the trichloromethyl radical with nitroso-compounds. Ultraviolet irradiation of solutions of benzoyl peroxide (BP) in CCl_4 or $CHCl_3$ as well as the photolysis of CCl_3Br in benzene in the presence of nitroso-compounds lead to the formation, together with other nitroxy-radicals, of radicals whose EPR spectrum is a triplet with $a_N = 6.5$ G and $g = 2.0070$.[63] These spectra were initially assigned to the spin-adducts of the $CCl_3^{\bullet}$ radical with nitroso-compounds[63]. The assignment was found to be erroneous when spectra of the nitroxy-radicals

$$CCl_3-N(\dot{O})-R$$

(IV)

were obtained in a number of studies with quite different hyperfine structures and hyperfine coupling constants (Table 2).

In one of the early investigations Chalfont[64] observed the formation of two long-lived radicals in the photolysis of CCl_3Br in the presence of MNP. One of these radicals was identified as the nitroxy-radical (IV), where $R = C(CH_3)_3$. It was erroneously assumed that the other radical, having $a_N = 6.65$ G, may be the bromine-containing nitroxy-radical $Br-N(\dot{O})-C(CH_3)_3$. This hypothesis was disproved when irradiation of CBr_4 in benzene in the presence of MNP led to a nitroxy-radical whose EPR spectrum had a similar constant $a_N = 6.5$ G, but contained a well resolved quartet with $a_{Br} = 2.1$ G.[47] On the basis of the results of Mackor et al.[30], Torssell[48] was the first to point out that the nitroxy-radicals with such a low constant a_N (6.5–6.7 G) probably have the structure of acylalkylnitroxy-radicals.

Subsequently Hartgerink et al.[63] reinvestigated the photolysis of CCl_4 and concluded[65] that the spectra under consideration (with $a_N = 6.5$ G and $g = 2.0070$) are due to the chlorocarbonylnitroxy-radicals (III). A well resolved splitting of the signal due to the β-chlorine in species of type (III) could never be detected.

The photolysis of CBr_4 in the presence of MNP leads to the formation of the bromocarbonylnitroxy-radical $Br-CO-N(\dot{O})-C(CH_3)_3$ with $a_N = 6.7$ G, $a_{Br} = 2.0$ G, and $g = 2.0071$.[65] These data were subsequently confirmed in yet another study[47]. The results quoted[47] for the photolysis of CCl_3Br show that the corresponding nitroxy-radicals (III) are undoubtedly formed in the presence of MNP or its perdeutero-derivative. Although the authors[47] assign the EPR spectrum (with $a_N = 6.65$ G and $a_{Hal} = 0.5$ G), obtained in the photolysis of CCl_3Br in the presence of a deuterated trapping agent, to the chlorine-containing radical nitroxy-radical (III) with Hal = Cl and $R = C(CD_3)_3$, adequate data for this assignment are not available and one cannot rule out the possibility of forming the bromocarbonylnitroxy-radical (III), with Hal = Br, or a mixture of two halogenocarbonylnitroxy-radicals. In particular, the above assignment conflicts with the observation[47] that the lines of the main ^{14}N triplet in the EPR spectrum of the nitroxy-radical obtained by the photolysis of CCl_3Br in the presence of MNP (Fig. 4) show a quartet splitting, which, although poorly resolved, is nevertheless sufficient to calculate a_{Hal}. On the basis of the spectrum obtained following the irradiation of bromotrichloromethane in the presence of MNP, Gasanov et al.[66] also determined the constants a_N = 6.7 G and a_{Br} = 2.2 G.

Figure 4. The EPR spectrum of the nitroxy-radical obtained on ultraviolet irradiation of CCl_3Br in the presence of MNP.[47]

This difference between the parameters of the spectra obtained on irradiation of CCl_4 and CCl_3Br may be attributed to the fact that in the latter case the $Cl-CO-N(\dot{O})-C(CH_3)_3$ spectrum is overlapped by another spectrum with similar parameters, but with a better resolution of the splitting in the quartet. It apparently corresponds to the nitroxy-radical $Br-CO-N(\dot{O})-C(CH_3)_3$.

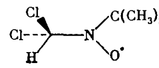
All the halogenocarbonylnitroxy-radicals obtained in the photolysis of bromotrichloromethane in the presence of trapping agents are therefore designated in Table 3 as $Hal-CO-N(\dot{O})-R$. The photolysis of CCl_4 or CCl_3Br in the presence of secondary nitroso-compounds (Table 3, Nos. 7–10) leads to the formation of the nitroxy-radicals $Cl-CO-N(\dot{O})-CHR_2$ whose spectrum shows splitting due to the β-hydrogen (a_H = 2.7–2.8 G).[63]

It has been suggested[47,65] that the nitroxy-radicals (III) are products of secondary reactions of the spin-adduct (IV) formed initially. The following evidence is quoted in support of this hypothesis: the gradual appearance of signals due to species (III) as the signals due to the adduct (IV) disappear, the high intensity of the signals in the spectra of (III), and the failure of the attempt to obtain (III) by the addition of the $Cl\dot{C}O$ radical (generated by the photolysis of phosgene or dibromocarbonyl in the presence of benzoyl peroxide) to MNP. Several possible versions of the mechanism of the above reaction are discussed in the studies indicated, but there has been no experimental confirmation of any of the suggested mechanisms.

(c) The $\dot{C}HCl_2$ and $\dot{C}H_2Cl$ radicals. The preparation of the spin-adducts of MNP with the $\dot{C}HCl_2$ and $\dot{C}H_2Cl$ radicals in the oxidation of 3-t-butyl-3-hydroxy-1-phenyltriazene by lead dioxide in CH_2Cl_2 and CH_2ClI respectively has been described[28] (Table 2, Nos. 11 and 14). In the first instance a multicomponent spectrum was obtained, whose analysis showed that the unpaired electron in the above spin-adduct interacts with the ^{14}N nucleus and the two equivalent chlorine nuclei. The spectrum contains lines which the authors assigned to the isotopic forms (V) and (VI):

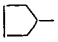
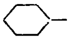
$$\underset{(V)}{H^{35}Cl_2C-N(\dot{O})-C(CH_3)_3}; \quad \underset{(VI)}{H^{35}Cl^{37}ClC-N(\dot{O})-C(CH_3)_3}.$$

The relative content of form (V) is 56.8% and that of (VI) 37.2%. The ratio of the hyperfine coupling constants $a_{^{37}Cl}/a_{^{35}Cl}$ = 0.83 is equal to the ratio of the magnetic moments $\mu_{^{37}Cl}/\mu_{^{35}Cl}$ = 0.832; hyperfine coupling with β-hydrogen was not observed. Similar observations were also made in a study[47] of the EPR spectrum of the nitroxy-radical $HCCl_2-N(\dot{O})-C(CD_3)_3$ (Table 2, No. 12). The absence of splitting by β-hydrogen was explained[28] by the fact that the preferred conformation



in which the proton is located in the plane of the molecule, is apparently formed in the given instance.

Table 3. Parameters of the EPR spectra of halogenocarbonylnitroxy-radicals (III).

№	R	Hal	a_N, G	Other HCC, G	Method of synthesis	Solvent	Refs.
1*	$(CH_3)_3C$	Cl	6.5	—	CCl_4 + MNP + BP + $h\nu$	CCl_4	63,65
2*	$(CH_3)_3C$	Cl	6.65	—	CCl_4 + MNP + BP + $h\nu$	CCl_4	47
3	$(CH_3)_3C$	Cl or Br	6.65	—	CCl_3Br + MNP + $h\nu$	CCl_3Br	47
4	$(CH_3)_3C$	Cl	6.5	—	CCl_4 + (cyclo- $C_6H_{11}OCO)_2$ + MNP	CCl_4	33,66
5	$(CH_3)_3C$	Cl or Br	6.7	a_{Hal}=2.2	CCl_3Br + $h\nu$	CCl_3Br	66
6	$(CD_3)_3C$	Cl or Br	6.65	a_{Hal}=0.5	CCl_3Br + $h\nu$	CCl_3Br	47
7**	1-Adamentyl	Cl or Br	6.5	$a_{H-\gamma}$=0.47	A***, B****, C*****	C_6H_6	63
8**	$(CH_3)_2CH$	Cl or Br	6.3	a_H=2.8	A, B, C	C_6H_6	63
9**		Cl or Br	6.4	a_H=2.8	A, B, C	C_6H_6	63
10**		Cl or Br	6.2	a_H=2.7	A, B, C	C_6H_6	63
11**	$(CH_3)_2CHC-(CH_3)_2$	Cl or Br	6.5	—	A, B, C	C_6H_6	63

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*g = 2.0070.

**It has been erroneously described[63] as $CCl_3-N(\dot{O})-R$ (see Refs. 65 and 47).

***CCl_4 + RNO + $h\nu$.

****$CHCl_3$ + $(C_6H_5COO)_2$ + RNO + $h\nu$.

***** CCl_3Br + RNO + $h\nu$.

The EPR spectrum of the nitroxy-radical $H_2CCl{-}N(\dot{O}){-}C(CH_3)_3$ consists of a superposition of the spectra of the two isotopic forms containing ^{35}Cl and ^{37}Cl. The spectrum includes lines corresponding to the interaction of the unpaired electron with the ^{14}N nucleus, the ^{35}Cl and ^{37}Cl nuclei, and the two equivalent protons[28] (Table 2, No. 14).

The $\dot{C}HCl_2$ radical, generated by the ultraviolet irradiation of methylene chloride in the presence of TBP, was also identified as the spin-adduct with 2-nitroso-2-trifluoromethylhexafluoropropane[22] (Table 2, No. 13). As for the spin-adduct of the same trapping agent with $\dot{C}Cl_3$, the value of a_N for the above compound is greater and that of a_{Cl} smaller than for the spin-adduct of the $\dot{C}HCl_2$ radical with MNP.

When hydrogen is abstracted from CH_2Cl_2 by the radicals formed in the decomposition of di-t-butyl peroxydioxalate at 30°C in the presence of perdeutero-2-methyl-2-nitrosopropane, the spectrum of the formyl derivative $HCO{-}N(\dot{O}){-}C(CD_3)_3$, for which $a_N = 7.0$ G and $a_H = 1.41$ G, was obtained togehter with that of the spin-adduct of the $\dot{C}HCl_2$ radical (Table 2, No. 12).[47]

3. Higher Chlorine-Containing Radicals

The study of higher radicals, containing one or two chlorine atoms at the radical centre, by the spin-trapping method in most cases involved the solution of chemical problems (see Section V), so that the examples compiled here do not constitute a systematic series. In all the cases investigated, MNP or its deutero-analogues were used to bind the $R\dot{C}Cl_3$ radicals.

The spectra of the spin-adducts of the $CHCl_2\dot{C}Cl_2$ radical with the above two trapping agents show a hyperfine structure due to the interaction of the unpaired electron with the ^{14}N nucleus and the nuclei of the two non-equivalent chlorine atoms (Table 4, Nos. 1 and 2). It has been suggested[47] that the non-equivalence of the chlorine atoms is associated with the high energy barrier to the rotation of two such atoms about the C–C bond in the tetrachloroethyl group. Theoretical analysis showed that the ratio of the constants $a_{^{35}Cl}$ and $a_{^{37}Cl}$ is in this case such that only components corresponding to the predominance of the form with two ^{35}Cl atoms should be detected in the EPR spectrum; the presence of other isotopic forms is revealed only by the "blurring" of the hyperfine structure of the spectrum[28].

The oxidation of 3-t-butyl-3-hydroxy-1-phenyltriazene in tetrachloroethylene takes place in an interesting manner[28]. It apparently entails the formation of the telomeric radicals $C_6H_5(CCl_2CCl_2)_n^{\cdot}$, which bind the MNP formed simultaneously; in this case it was also possible to detect the splitting by the ^{35}Cl and ^{37}Cl nuclei (Table 4, No. 5).

It has been shown[33,66] that, in the system of radicals formed via a rearrangement according to the scheme

$$\underset{(VII)}{XCH_2\dot{C}HCCl_3} \xrightarrow{\varrho} \underset{(VIII)}{XCH_2CHCl\dot{C}Cl_2}\ ,$$

$$X = CCl_3 \text{ or } (CH_3)_3CO \qquad (13)$$

the radicals (VIII) combined selectively with MNP and did not give rise to a stable spin-adduct with MNB, while the radicals (VII) gave rise to an EPR spectrum in the presence of MNB but not in the presence of MNP. These two trapping agents behave similarly also in relation to the radicals (IX) and (X), which are present simultaneously in solution[51]:

$$\underset{(IX)}{XCH_2\dot{C}HCCl_2F} \xrightarrow{\varrho} \underset{(X)}{XCH_2CHCl\dot{C}ClF}\ ,$$

$$X = CCl_3 \text{ or } CHCl_2\ . \qquad (14)$$

Table 4. Parameters of the EPR spectra of $R{-}N(\dot{O}){-}C(CH_3)_3$ nitroxy-radicals (spin-adducts of MNP with higher radicals containing chlorine at the radical centre).

№	R	a_N, G	a_{Cl}, G	Other HCC, G	Method of generation of radicals	Temp., °C	Refs.
1	$HCCl_2CCl_2$	12.8	Cl_1 : 4.50; Cl_2 : 0.80	—	$CHCl_2CHCl_2 + C_6H_5N = N{-}N(OH){-}C(CH_3)_3 + PbO_2$	room	28
2*	$HCCl_2CCl_2$	12.75	Cl_1 : 4.5; Cl_2 : 1.1	—	$CHCl_2CHCl_2$ + di-t-butyl peroxydioxalate	30	47
3**	$CCl_3CH_2CHClCCl_2$	12.4	2.2	—	$CCl_3Br + CH_2 = CHCCl_3 + h\nu$	25	33, 66
4**	$(CH_3)_3COCH_2CHClCCl_2$	12.4	2.2	—	$TBP + CH_2 = CHCCl_3 + h\nu$	25	33
5	$C_6H_5(CCl_2CCl_2)_n$	12.0	4.2; 3.5****	—	$CCl_2 = CCl_2 + C_6H_5N = N{-}N(OH){-}C(CH_3)_3 + PbO_2$	room	28
6	$CCl_3CH_2CHClCFCl$	14.1	4.1	$a_F = 1.6$	$CHCl_3 + CH_2 = CHCCl_2F + TBP + h\nu$	55—60	87
7	$CCl_3CH_2CHClCFCl$	14.0	4.1	$a_F = 1.5$	$CCl_4 + CH_2 = CHCCl_2F + (C_2H_5)_3SiH + TBP + h\nu$	55—60	87
8	$CHCl_2CH_2CHClCFCl$	14.4	4.3	$a_F = 1.6$	$CH_2Cl_2 + CH_2 = CHCCl_2F + TBP + h\nu$	55—60	87
9	$CH_2ClCHCl$	12.1	7.0; 5.8****	—	$CH_2ClCH_2Cl + C_6H_5N = N{-}N(OH){-}C(CH_3)_3 + PbO_2$	room	28
10	$(CH_3)_2CCl$	12.1	7.0; 5.8****	—	$(CH_3)_2CHCl + C_6H_5N = N{-}N(OH){-}C(CH_3)_3 + PbO_2$	room	28
11**	$CCl_3CH_2CHClCHCl$	14.3	3.6	$a_H = 1.7$	$CCl_4 + CH_2 = CHCHCl_2 + (C_2H_5)_3SiH + TBP + h\nu$	55—60	87
12	$HOOCCHCl$	12.5	5.5	$a_H = 1.1$	$CHClBrCOOH + (C_6H_5)_3SiH + TBP + h\nu$	25	88
13***	$C_6H_{13}CH_2CCl$ $\quad\;\; \vert$ $\quad COOH$	14.2	0.8	—	$C_8H_{16} + CHClBrCOOH + TBP + h\nu$	room	88

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*Trapping agent—$(CD)_3CNO$.

**Formed as a result of rearrangement with 1,2-migration of chlorine atoms.

***Formed as a result of rearrangement with 1,3-migration of hydrogen atoms.

****The values of a_{Cl} for ^{35}Cl and ^{37}Cl respectively.

According to the results of Camaggi et al.[47], the interaction of t-butoxy-radicals with 1,1-dichloroethane and αα-dichlorotoluene in the presence of MNP yielded EPR spectra characteristic of acetyl- and benzoyl-t-butylnitroxy-radicals respectively, and not of chlorine-containing nitroxy-radicals.

The nitroxy-radicals $CH_2ClCHCl-N(\dot{O})-C(CH_3)_3$ (Table 4, No. 9), in the EPR spectrum of which there is no splitting by β-hydrogen, was obtained by the oxidation of aryloxytriazene with lead dioxide in dichloroethane[28]. The authors suggest that the hydrogen atom in this nitroxy-radical is close to the nodal plane of the *p*-orbital of the nitrogen atom occupied by the unpaired electron. In this arrangement the extent of the interaction of the unpaired electron with β-hydrogen is a minimum.

IV. EPR SPECTRA OF NITROXY-RADICALS—SPIN-ADDUCTS OF SULPHUR-CONTAINING RADICALS

The study of the free radicals formed as intermediates in various reactions of organosulphur compounds under the influence of ultraviolet and γ-radiation or of thermal initiation is of great importance both for the elucidation of the mechanisms of such processes and for the solution of problems which are extremely important from a practical point of view[55,67].

However, direct detection of thiyl radicals by EPR in the liquid phase is evidently impossible owing to their π-orbital degeneracy[68,69]. Furthermore, recent studies have shown that RS$^{\cdot}$ radicals cannot be investigated by EPR in the solid phase: many of the earlier reports apparently refer to the dimeric species $RS^{\cdot}SR_2$ and not to RS$^{\cdot}$ radicals[68].

The spin-trapping method makes it possible to obviate these difficulties and its use for the identification of sulphur containing radicals is apparently of particular interest. Fairly numerous examples of the study of a wide variety of sulphur-containing radicals by this method are now known. The radicals investigated can be arbitrarily divided into three groups: (1) thiyl radicals RS$^{\cdot}$, (2) sulphonyl radicals $RSO_2^{\cdot}$, and (3) other radicals in which the unpaired electron is at a carbon or oxygen atom (C and O radicals), while the sulphur-containing group is attached to a β- or γ-carbon atom.

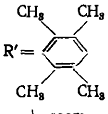
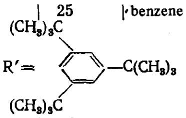
The data discussed below illustrate examples of the investigation of sulphur-containing radicals of each of these three types with the aid of spin-trapping agents. Comparison of these results shows that the EPR spectra of thiyl- and sulphonyl-nitroxy-radicals, $RS-N(\dot{O})-R'$ and $RSO_2-N(\dot{O})-R'$, are characterised in the general case only by a ^{14}N triplet, but the values of a_N and of the *g*-factor can frequently serve as adequate criteria for the identification of these nitroxy-radicals.

1. The Thiyl Radicals

The first attempt to identify by EPR free radicals with an unpaired electron at a sulphur atom in the form of spin-adducts with a trapping agent (MNP) was undertaken in 1968.[70] Solid polycrystalline specimens of various aminoacids were γ-irradiated and then dissolved in an aqueous solution of MNP and placed in the resonator of the EPR spectrometer. However, in contrast to all other examples, sulphur-containing aminoacids (cysteine, cystine, and methionine) altogether failed to give rise to any EPR signals under these conditions. This enabled the authors to conclude that the adducts of the RS$^{\cdot}$ radicals with MNP are evidently much less stable than the adducts of C radicals.

A study was therefore made of the possibility of identifying with the aid of MNP the thiyl radicals formed on photolysis of thiols and disulphides directly in the resonator of the spectrometer[31]. The RS$^{\cdot}$ radicals were generated by irradiating solutions of butane-1-thiol or di-n-butyl sulphide in oxygen-free heptane with light having λ = 245 and 300 nm respectively. It was possible to avoid in this way the secondary formation of the di-t-butylnitroxy-radical from MNP, which complicates the EPR spectrum (see Section II). When dibutyl disulphide was irradiated in the presence of MNP, a spectrum consisting of a triplet with a_N = 18.52 G and *g* = 2.0071 was obtained. The authors assigned it to the spin-adduct of the $C_4H_9S^{\cdot}$ radicals with the trapping agent. The adduct (Table 5, No. 10) indeed proved to be very unstable: the EPR signals disappeared almost immediately after irradiation ceased. Apart from the above triplet, the spectrum showed another less intense triplet with a_N = 14.93 G and *g* = 2.0058, the origin of which the authors could not establish. After the irradiation of butanethiol, the triplet corresponding to the spin-adduct of the $C_4H_9S^{\cdot}$ radical was also detected[31,59].

Table 5. Parameters of the EPR spectra of the $RS-N(\dot{O})-R'$ nitroxy-radicals (spin-adducts of thiyl radicals).

№	RS	a_N, G	*g*-Factor	Method of generation of radicals	Temp., °C	Solvent	Refs.
Trapping agent--MNP, $R'=C(CH_3)_3$							
1*	CH_3S	18.9	2.0064	$CH_3SH+h\nu$	—103	CH_3SH	73
2	C_2H_5S	17.4	2.0063	$C_2H_5SH+h\nu$	—92	C_2H_5SH	73
3	C_3H_7S	17.8	2.0063	$C_3H_7SH+h\nu$	—85	C_3H_7SH	73
4	iso-C_3H_7S	16.7	2.0062	iso-$C_3H_7SH+h\nu$	—97	iso-C_3H_7SH	73
5	iso-C_3H_7S	16.99	2.0068	$(iso\text{-}C_3H_7)_2S+$ $+(C_6H_5)_2CO+h\nu$	room	—	71
6	iso-C_3H_7S	16.99	2.0068	$(iso\text{-}C_3H_7)_2S_2+h\nu$	room	$(iso\text{-}C_3H_7)_2S_2$	71
7	C_4H_9S	17.8	2.0063	$C_4H_9SH+h\nu$	—73	C_4H_9SH	73
8	C_4H_9S	18.5	2.0071	$C_4H_9SH+h\nu$	room	heptane	31
9	C_4H_9S	18.52	2.0071	$C_4H_9SH+h\nu$	room	heptane	59
10	C_4H_9S	18.52	2.0071	$(C_4H_9)_2S_2+h\nu$	room	heptane	31
11	C_4H_9S	18.21	2 0070	$(C_4H_9)_2S_2+$ $+(C_6H_5)_2CO+h\nu$	room	—	71
12	C_6H_5S	16.75	2.0066	C_6H_5SH+ $+(C_6H_5)_2CO+h\nu$	room	benzene	71
13	C_6H_5S	16.5	2.0066	$C_6H_5C(SC_6H_5)_2CH_3+$ $+h\nu$	—65÷—25	CH_2Cl_2	74, 75
Trapping agent--nitrosodurene, R′= 							
14	CH_3S	16.48	2.0068	$(CH_3)_2S_2+h\nu$	room	benzene	35
15	C_3H_7S	16.82	2.0068	$(C_3H_7)_2S_2+h\nu$	room	benzene	35
16	C_6H_5S	16.01	2 0065	$(C_6H_5)_2S_2+h\nu$	room	benzene	35
Trapping agent--nitrosobenzene, $R'=C_6H_5$							
17**	C_6H_5S	11.42	2.0059		25	benzene	76
Trapping agent--2,4,6-tri-t-butylnitrobenzene, R′= 							
18***	C_6H_5S	16.29	2.0066	$(C_6H_5)_2S_2+h\nu$	25	benzene	36

$^{*}a_{H(CH_3)}$ = 1.2 G.
$^{**}a_{H\text{-}o} = a_{H\text{-}p}$ = 2.52 G; $a_{H\text{-}m}$ = 0.86 G.
$^{***}a_{H\text{-}m}$ = 0.85 G.

The EPR spectra of the spin-adducts of other thiyl radicals (iso-$C_3H_7S^{\cdot}$, $C_6H_5S^{\cdot}$) with MNP were observed by the same workers[71] in the photochemical reduction of benzophenone by thiols and sulphides. The spectra consisted of triplets having similar g-factors and a_N constants in the range 16.5–18.5 G (Table 5, Nos. 5, 6, 11, and 12).

It is noteworthy that, when thiophenol is used for the photochemical reduction of benzophenone in the presence of MNP, the formation of not only the $C_6H_5S-N(\dot{O})-C(CH_3)_3$ nitroxy-radical, but also of the $H-N(\dot{O})-C(CH_3)_3$ t-butylnitroxy-radical (which may be formally regarded as the spin-adduct of a hydrogen atom and MNP), whose spectrum has $a_N = 13.6$ G, $a_{H(NH)} = 12.36$ G, and $g = 2.0062$, was observed[71]. It is of interest to compare with this result a study[72] where it was shown that thiophenol is reduced to a nitroso-compound on ultraviolet irradiation:

$$2RNO + 2C_6H_5SH \rightarrow 2R-N(\dot{O})-H + (C_6H_5S)_2 \quad . \qquad (15)$$

The EPR spectrum then shows (for $R = t\text{-}C_4H_9$) a triplet of doublets with $a_N = 13.1$ G, $a_H^{NH} = 11.2$ G, and $g = 2.0063$. The authors[72] do not mention the formation under these conditions of the t-butylphenylthionitroxy-radical, but it is seen from the spectrum quoted in their paper that it is formed: the spectrum shows a low-intensity triplet with $a_N = 16.6$ G.

The spectra of the spin-adducts of MNP with different aliphatic RS˙ radicals (Table 5, Nos. 1–4 and 7) have been recently described by Wargon and Williams, who investigated the γ-radiolysis of thiols, sulphides and disulphides at temperatures between −50° and −110°C.[73] The constants a_N and the g-factors which they obtained (16.7–18.9 G and 2.0062–2.0064) are close to those quoted above. It is noteworthy that the spectrum of the spin-adduct of the $CH_3S^{\cdot}$ radical shows clearly the splitting of the lines of the ^{14}N triplet into quartets due to the interaction with the hydrogen atoms of the methyl group ($a_H = 1.2$ G; Table 5, No. 1). For other RS˙ radicals, the splitting of the signals by hydrogen atoms is much less intense, and the hyperfine coupling is manifested solely by increased width of the lines of the main triplet.

The characteristic constant $a_N = 16.5$–18.5 G can serve as a criterion of the assignment of such a triplet in the EPR spectrum to the spin-adducts of MNP with thiyl radicals. Another characteristic feature of the spectra of these spin-adduct is the rapid disappearance of the signal after irradiation has been stopped, i.e. the low stability of the radical. For example, these data enabled the authors[74,75] to assign the triplet with $a_N = 16.5$ G, observed in the complex EPR spectrum during the photolysis of acetophenone diphenylmercaptal, to the spin-adduct of the $C_6H_5S^{\cdot}$ radical with MNP (Table 5, No. 13; see also Section V).

Because of the ease of the generation of thiyl radicals from disulphides and thiols, many systematic studies devoted to the investigation of new spin-trapping agents contain data about the adducts of RS˙ radicals with such agents. For example, the detection of thiyl radicals with the aid of nitrosodurene[35], nitrosobenzene[76], and 2,4,6-tri-t-butylnitrosobenzene[36] has been described (Table 5, Nos. 14–18). The nitroxy-radicals formed under these conditions have relatively high values of a_N.

It is seen from the data presented that thiylalkyl- and thiylaryl-nitroxy-radicals are in general characterised by higher values of a_N than dialkyl- and alkylaryl-nitroxy-radicals and by a g-factor which is appreciably displaced downfield compared with that of the free electron. This can be apparently accounted for by the fact that the spin-orbital coupling constant for heteroatomic substituents such as sulphur is fairly considerable (approximately 382 cm⁻¹).[31]

The data at present available also make possible the conclusion that neither temperature nor the solvent have a significant influence on the parameters of the spectra of thiylnitroxy-radicals.

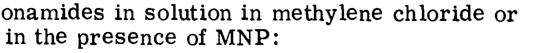
Table 6. Parameters of the EPR spectra of $RSO_2-N(\dot{O})-C(CH_3)_3$ nitroxy-radicals [MNP spin-adducts (in benzene at room temperature)].

№	RSO_2	a_N, G	Method of generation of radicals	Refs.
1*	$C_6H_5SO_2$	12.2	see Schemes (16) and (17) in text	78
2	$p\text{-}CH_3C_6H_4SO_2$	12.5	$CH_3C_6H_4SO_2I$ + see also Schemes (18) and (19) in text	40
3	$C_6H_5SO_2$	12.0	$C_6H_5SO_2Cl + h\nu$	51, 52
4	$C_6H_5SO_2$	12.2	$C_6H_5SO_2F + (C_2H_5)_3SiH +$ TBP $+ h\nu$	51, 52
5	$C_6H_5SO_2$	12.1	$C_6H_5SO_2Br + h\nu$	52
6	$C_2H_5SO_2$	12.2	$C_2H_5SO_2Cl + h\nu$	51
7	$C_2H_5SO_2$	12.2	$C_2H_5SO_2Cl + (CH_3COO)_2 + h\nu$	51
8	$ClSO_2$	11.7	$C_6H_5SO_2Cl + h\nu$	51, 52
9	$ClSO_2$	11.6	$SO_2Cl_2 + h\nu$	51, 52
10	FSO_2	12.4	$C_6H_5SO_2F + h\nu$	51, 52
11	FSO_2	12.6	$SO_2FCl + h\nu$	51, 52
12	$BrSO_2$	11 9	$C_6H_5FO_2Br + h\nu$	52

*$g = 2.0061$; the parameters of the EPR spectra of a large number of $RSO_2-N(\dot{O})-R'$ nitroxy-radicals have also been published by Wajer et al.[78], but, since they were obtained by procedures other than the spin-trapping method, they are not considered here.

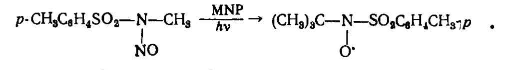
2. Sulphonyl Radicals

The EPR spectrum of the $RSO_2-N(\dot{O})-R'$ nitroxy-radical ($R = R' = CH_3$) was obtained for the first time by Lagercrantz[77]. The spectrum was recorded in a study of the reaction of dimethyl sulphoxide with nitrogen dioxide. The assignment was based on the hyperfine structure: the lines of the main ^{14}N triplet are split owing to hyperfine coupling with two non-equivalent H atoms of the methyl group ($a_H = 11.0$ G and $a_{H'} = 0.094$ G). The values of a_N and the g-factor for the spectra of radicals of this type (12.2 G and 2.0059 respectively) were obtained for the first time. The validity of this assignment was fully confirmed in a study[78] where the spectra of a number of sulphonylnitroxy-radicals of the above type (R = aryl and R′ = alkyl, phenyl, phenylsulphonyl, etc.) were investigated. These nitroxy-radicals were obtained either by the oxidation of N-alkyl- or N-aryl-benzenesulphonylhydroxylamines by lead dioxide:

 (16)

$$RNO + C_6H_5SO_2H \rightarrow R-\underset{\substack{|\\OH}}{N}-SO_2C_6H_5 \xrightarrow{PbO_2} R-\underset{\substack{|\\O^{\cdot}}}{N}-SO_2C_6H_5 \quad , \qquad (16)$$

or by the photolysis of N-methyl-N-nitrosotoluene-p-sulphonamides in solution in methylene chloride or toluene in the presence of MNP:

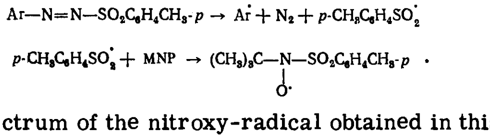
 (17)

$$p\text{-}CH_3C_6H_4SO_2-\underset{\substack{|\\NO}}{N}-CH_3 \xrightarrow[h\nu]{MNP} (CH_3)_3C-\underset{\substack{|\\O^{\cdot}}}{N}-SO_2C_6H_4CH_3\text{-}p \quad . \qquad (17)$$

The spectra of the resulting nitroxy-radicals are characterised by the constants $a_N = 11$–12 G (a_N is somewhat less than 10.1 G only for the bisbenzenesulphonylnitroxy-radical) and $g = 2.0061$ (Table 6, No. 1). Such a high value of a_N is unusual for nitroxy-radicals with powerful electron-accepting substituents of this kind (for example $a_N = 4-5$ G for diacylnitroxy-radicals)[15]. The authors[78] explain this by the fact that the nitrogen in sulphonylnitroxy-radicals has a pyramidal structure, and the unpaired electron occupies an orbital with enhanced s-character.

Unfortunately the authors of the above investigations say nothing about the stability of the sulphonylnitroxy-radicals investigated, which is an important characteristic of the spin-adducts in the spin-trapping method.

The detection of toluene-*p*-sulphonyl radicals with the aid of MNP was also noted in the photolysis and thermolysis of *p*-tolyl arylazo sulphones[40]:



$$\mathrm{Ar{-}N{=}N{-}SO_2C_6H_4CH_3\text{-}}p \rightarrow \mathrm{\dot{Ar}} + \mathrm{N_2} + p\text{-}\mathrm{CH_3C_6H_4SO_2^{\cdot}}$$

$$p\text{-}\mathrm{CH_3C_6H_4SO_2^{\cdot}} + \mathrm{MNP} \rightarrow \mathrm{(CH_3)_3C{-}\underset{\displaystyle \underset{|}{} \atop O^{\cdot}}{N}{-}SO_2C_6H_4CH_3\text{-}}p \quad . \qquad (18)$$

The spectrum of the nitroxy-radical obtained in this way had $a_N = 12.5$ G and $g = 2.0061$. To confirm this assignment, the same nitroxy-radical was obtained by an independent procedure: by the photolysis of toluene-*p*-sulphonyl iodide in the presence of MNP (Table 6, No.2). The authors note a very low stability of this nitroxy-radical—its half-life is only 44 s, so that its spectrum disappears rapidly after irradiation ceases. The formation of the same nitroxy-radical has been noted[79] in the detection with the aid of MNP of toluene-*p*-sulphonyl radicals generated via the mechanism.

$$\begin{aligned}
&[\mathrm{(CH_3)_3COOCO}]_2 \rightarrow 2\,\mathrm{(CH_3)_3C\dot{O}} + 2\mathrm{CO_2} \quad ,\\
&\mathrm{(CH_3)_3C\dot{O}} + \mathrm{(C_4H_9)_3SnH} \rightarrow \mathrm{(CH_3)_3C\dot{O}H} + \mathrm{(C_4H_9)_3Sn^{\cdot}} \quad ,\\
&\mathrm{(C_4H_9)_3Sn^{\cdot}} + p\text{-}\mathrm{CH_3C_6H_4SO_2Cl} \rightarrow \mathrm{(C_4H_9)_3SnCl} + p\text{-}\mathrm{CH_3C_6H_4SO_2^{\cdot}} \quad . \qquad (19)
\end{aligned}$$

The photochemical decomposition of benzenesulphonyl halides $C_6H_5SO_2Hal$ (Hal = F, Cl, or Br) was investigated by the spin-trapping method[51,52]. These compounds may decompose both at the C–S and at the S–Hal bonds[80]. This can lead to the formation of either $C_6H_5SO_2^{\cdot}$ or $HalSO_2^{\cdot}$ radicals, or both. The adducts of these radicals with MNP should give rise to triplets with similar values of a_N in the EPR spectra. Nevertheless, the employment of independent methods for the generation of these radicals (for example, $ClSO_2^{\cdot}$ from SO_2Cl_2, $FSO_2^{\cdot}$ from SO_2FCl, etc.) and allowance for the different stabilities of the corresponding spin-adducts enabled the authors[51,52] to make unambiguous assignments of the EPR spectra (Table 6, Nos. 3–12, see also Section V).

Thus one may conclude that $RSO_2^{\cdot}$ radicals may be identified with the aid of the spin-trapping method, and the differences between the stabilities of their spin-adducts can serve as additional information in the assignment of extremely similar signals in the EPR spectra of the latter.

There are no literature data for other trapping agents used in the detection of sulphonyl radicals. One can only note that, in the photolysis of SO_2Cl_2 in the presence of t-butyl phenyl nitrone, it is possible to detect only the adduct of a chlorine atom with the trapping agent[52]; the $ClSO_2^{\cdot}$ radical evidently does not give rise to stable spin-adducts with the nitrone.

In the study of radical reactions of various sulphones (initiated by the $\dot{O}H$ radicals formed in the photolysis of hydrogen peroxide), in the presence of MNP and MNB as trapping agents, it is impossible to detect the spin-adducts of the sulphonyl radicals[81]. Some of the sulphones investigated totally failed to give rise to radical signals visible in the EPR spectrum, while others formed radicals by abstraction of a hydrogen atom from the methylene group adjoining the sulphonyl group (these were in fact detected by the trapping agents)[81]. It is of interest to note that, under these conditions, the sulphoxides R_2SO give rise to alkyl radicals $R^{\cdot}$ (identified from the spectra of their spin-adducts)[81]. On this basis, the authors[82,83] developed a method for the radical alkylation of aromatic and heteroatomic compounds by sulphoxides.

3. Other Sulphur-Containing Radicals

In the study of the radical reactions of organosulphur compounds by the spin-trapping method the formation of the spin-adducts of not only $\dot{S}$ radicals, but also of sulphur-containing $\dot{C}$ radicals is frequently noted. For example, in a study, already mentioned above[71] the $(CH_3)_2\dot{C}{-}S{-}CH(CH_3)_2$ radicals were detected (as their spin-adducts with MNP) together with iso-$C_3H_7S^{\cdot}$ radicals in the photochemical reduction of benzophenone by isopropyl sulphide. The formation of $\dot{C}$ radicals ($\dot{C}H_2SH$, etc.), identified from the spectra of their spin-adducts, was also noted in the γ-radiolysis of thiols[73] below −70°C. Apart from the $C_6H_5S^{\cdot}$ radicals, other sulphur-containing $\dot{C}$ and $\dot{O}$ radicals were detected in the photochemical reactions of acetophenone diphenylmercaptal[74,75] (Table 7, Nos. 1–6). This reaction is discussed in greater detail in Section V.

The data presented in Table 7 show that the constants a_N for the MNP adducts with $\dot{C}$ radicals containing the thiyl group in the β-position vary in the range 12–15 G, which is in general characteristic of dialkylnitroxy-radicals[16,84]. The adducts of MNP with $\dot{C}$ radicals containing the SO_2Cl group in the β-position have a much lower value of a_N (approximately 7 G; see Table 7, No. 7), i.e. of the same order of magnitude as for acylalkylnitroxy-radicals[85].

With the exception of isolated examples, there have so far been no studies of the possibility of the selective detection of particular organosulphur radicals with the aid of various spin-trapping agents (virtually all the investigations have been carried out solely with MNP), but this approach may prove to be extremely promising in this field also.

V. THE APPLICATION OF THE SPIN-TRAPPING METHOD IN THE STUDY OF THE MECHANISMS OF CERTAIN REACTIONS OF ORGANOCHLORINE AND ORGANOSULPHUR COMPOUNDS

This Section deals with examples, which have already been partly considered, where spin-trapping agents were used to investigate complex radical reactions of organochlorine and organosulphur compounds. The experimental facts accumulated in systematic studies (i.e. in those where radicals of known structure were detected with the aid of spin-trapping agents and the parameters of the EPR spectra of the corresponding spin-adducts were described) made it possible to assign them subsequently on the basis of the parameters of the observed EPR spectra to the spin-adducts of particular radicals formed in the course of a chemical reaction. Radical reactions include, as a rule, the intermediate formation of various radicals (owing to chain propagation and transfer, rearrangements, etc.). If these reactions are carried out in the presence of spin-trapping agents, very complex EPR spectra, corresponding to a mixture of various nitroxy-radicals, are therefore observed. The individual lines are then frequently superimposed, which greatly

Table 7. Parameters of the EPR spectra of R–N(Ȯ)–C$(CH_3)_3$ nitroxy-radicals (spin-adducts of MNP with sulphur-containing radicals).

№	R	a_N, G	Method of generation of radicals	Temp., °C	Solvent	Refs.
1*	$(CH_3)_3CSCH(CH_3)_2$	14.21	$(iso\text{-}C_3H_7)_2S + (C_6H_5)_2CO + h\nu$	room		71
2**	$C_6H_5SCH_2$	13.83	$C_6H_5SCH_3 + (C_6H_5)_2CO + h\nu$	room		71
3***	$C_6H_5C(SC_6H_5)_2CH_2$	14.3	$C_6H_5C(SC_6H_5)_2CH_3 + h\nu$	10—25	CH_2Cl_2	74,75
4	$C_6H_5C(SC_6H_5)CH_2SC_6H_5$	11.9 12.1	$C_6H_5C(SC_6H_5)_2CH_3 + h\nu$	room	CH_2Cl_2 CCl_4	74,75
5	$C_6H_5C(SC_6H_5)CH_2SC_6H_5$	12.0	$C_6H_5CH(SC_6H_5)CH_2SC_6H_5 +$ TBP $+ h\nu$	room	CH_2Cl_2, CCl_4	74,75
6	$C_6H_5\underset{\underset{O}{\vert}}{C}(SC_6H_5)CH_3$	25.7	$C_6H_5C(SC_6H_5)_2CH_3 + h\nu$	—50—65	CH_2Cl_2	74,75
7****	CH_3CHSO_2Cl	6.9	$C_2H_5SO_2Cl + (CH_3COO)_2 + h\nu$	room	Benzene	51

*$g = 2.0061$.

**$g = 2.0064$; $a_{H(CH_2)} = 5.9$ G.

***$a_{H(CH_2)} = 7.6$ G.

****$a_{H(CH)} = 1.5$ G.

hinders the interpretation of the spectrum. However, certain procedures which make it possible to simplify this task have been used recently.

1. The Selectivity of Spin-Trapping Agents

It was already noted above (see Section II) that certain spin-trapping agents are capable of detecting particular short-lived radicals to different extents. The selectivity of various spin-trapping agents in relation to radicals of different types has been used by the present authors[33]. As shown previously[86], a study of the rearrangement of polychloroalkyl radicals with 1,2-migration of the chlorine atom in accordance with Eqn.(13) yielded spectroscopic proof of the simultaneous presence in the reaction mixture of both radicals—the rearranged radical (VIII) and the non-rearranged radical (VII). Fig. 5 illustrates the EPR spectra obtained in the photochemically initiated reaction of TBP with 3,3,3-trichloropropene in the presence of MNP and MNB. Fig. 5 shows that MNP detects selectively only the rearranged radical (VIII); for X = $(CH_3)_3CO$, the spectrum with the characteristic splitting by the two β-chlorine atoms corresponds to the $(CH_3)_3COCH_2CHClCCl_2$–N(Ȯ)–C$(CH_3)_3$ nitroxy-radical (Table 4, No. 4), while MNB combines only with the non-rearranged radical (VII): the spectrum with doublet splitting by β-hydrogen corresponds to the $(CH_3)_3COCH_2CH(CCl_3)$–N(Ȯ)–C$(CH_3)_2COCH_3$ radical. Analogous results were obtained also in other instances of the rearrangement of radicals with 1,2-migration of chlorine[86,87].

The use of the selectivity of spin-trapping agents also permitted the study of the photochemical decomposition of various sulphonyl halides[51,52]. It was shown, for example, that SO_2Cl_2 decomposes on ultraviolet irradiation into $ClSO_2^{\bullet}$ radicals and $Cl^{\bullet}$ atoms, the former being selectively detected by MNP and the latter by BPN. The decomposition of benzenesulphonyl chloride involves the dissociation of the C–S bond together with that of the S–Cl bond[51,52]:

$$C_6H_5SO_2Cl \rightarrow C_6H_5^{\bullet} + ClSO_2^{\bullet} \quad . \qquad (20)$$

Phenyl radicals were detected with the aid of BPN and chlorosulphonyl radicals were detected with the aid of MNP.

The available data do not as yet show why certain trapping agents are incapable of detecting particular radicals. This can probably be accounted for by two causes: either the trapping agent does not react with the radical owing to unfavourable polar or steric effects or the spin-adduct formed is insufficiently stable for its identification by EPR. Nevertheless, the above purely empirical approach to the study of radical reactions, using the selectivity of various spin-trapping agents, appears to be extremely convenient and promising.

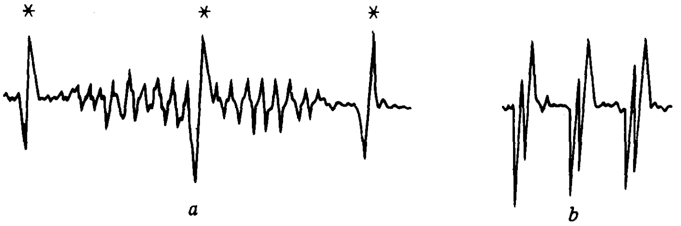


Figure 5. The ESP spectra of the nitroxy-radicals formed in the photochemical reaction of TBP with 3,3,3-trichloropropene[33]: *a*) in the presence of MNP (the triplet corresponding to the spin-adduct of MNP with t-butoxy-radicals is designated by asterisks); *b*) in the presence of 2-methyl-2-nitroso-3-butanone.

2. The Different Stabilities of Spin-Adducts

It was already noted previously that the adducts of spin-trapping agents, particularly of MNP, with various radicals have different stabilities. The time required for the disappearance of their signals from the EPR spectrum varies from several seconds to many hours. The possibility therefore arises of identifying certain radicals present in a mixture with other radicals by recording the

EPR spectrum immediately at the beginning of the reaction and after some time. The initial complex spectrum in some instances becomes greatly simplified owing to the destruction of less stable nitroxy-radicals.

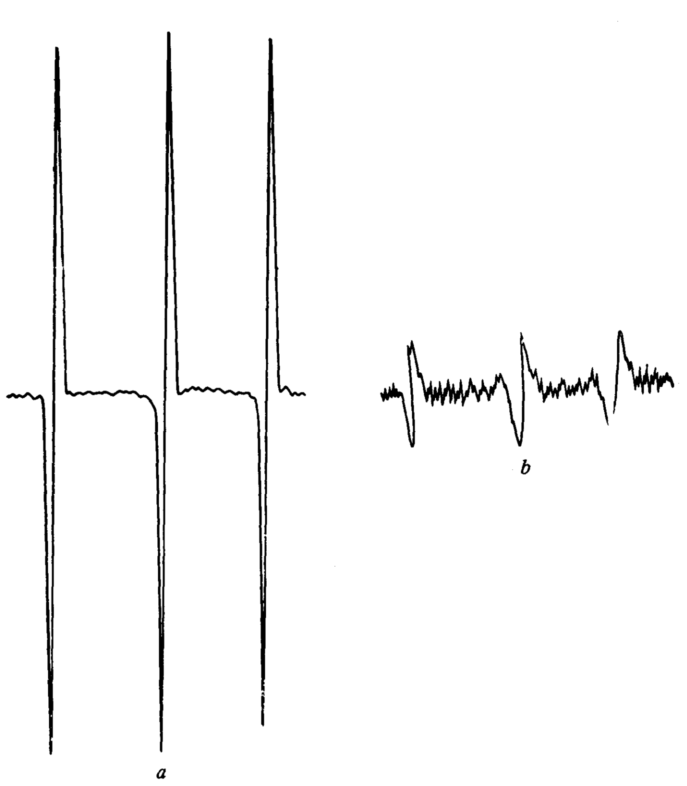


Figure 6. The EPR spectrum of a benzene solution of $C_6H_5SO_2Cl$ [52]: *a*) on ultraviolet irradiation; *b*) 2 min after the cessation of irradiation.

This procedure has been used successfully[51,52]. Ultraviolet irradiation of a benzene solution of benzenesulphonyl chloride in the presence of MNP gave an EPR spectrum consisting of a triplet with a_N = 12.0 G (Fig. 6*a*). When 2 min elapsed from the cessation of irradiation, the spectrum showed a much less intense triplet with a_N = 11.7 G (Fig. 6*b*); subsequently its intensity did not change for at least 30 min. This suggested that the triplet in Fig. 6*a* is a result of the superposition of signals due to two different nitroxy-radicals with similar values of a_N. Such nitroxy-radicals might be the spin-adducts of MNP with the $C_6H_5SO_2^{\cdot}$ and $ClS_2^{\cdot}$ radicals. By generating these radicals using independent methods [Schemes (21) and (22)] in the presence of MNP,

$$\begin{gathered} SO_2Cl_2 \xrightarrow{u,v,} \dot{S}O_2Cl + Cl^{\cdot} \quad , \\ \dot{S}O_2Cl + MNP \rightarrow \underset{(XI)}{ClSO_2 - N(\dot{O}) - C(CH_3)_3} \quad ; \end{gathered} \qquad (21)$$

$$\begin{gathered} C_6H_5SO_2Cl + [(CH_3)_3CO]_2 + (C_2H_5)_3SiH \xrightarrow{2537 Å} C_6H_5SO_2^{\cdot} + (CH_3)_3COH + (C_2H_5)_3SiCl \quad , \\ C_6H_5SO_2^{\cdot} + MNP \rightarrow \underset{(XII)}{C_6H_5SO_2 - N(\dot{O}) - C(CH_3)_3} \quad ; \end{gathered} \qquad (22)$$

it was shown that the nitroxy-radical (XI) is stable for a long time, while the signals due to the nitroxy-radical (XII) vanish almost immediately after irradiation ceases. The conclusion that the photochemical decomposition of benzenesulphonyl chloride involves the dissociation of both C–S and S–Cl bonds was thus confirmed[51,52].

The different stabilities of the spin-adducts of MNP also permitted the elucidation of the mechanism of another extremely complex reaction—the addition of bromochloroacetic acid to oct-1-ene with photochemical initiation. This process can be represented by the following scheme[88]‡:

$$\text{Initiator} \longrightarrow R^{\cdot} \quad ,$$

$$R^{\cdot} + HOOCCHClBr \longrightarrow RBr + \underset{(XIII)}{HOOC\dot{C}HCl} \quad ,$$

$$(XIII) + CH_2{=}CHC_6H_{13} \longrightarrow \underset{(XIV)}{HOOCCHClCH_2\dot{C}HC_6H_{13}} \quad ,$$

$$(XIV) \begin{cases} \xrightarrow{\circ\ 1,3\text{-}H} \underset{(XV)}{HOOC\dot{C}ClCH_2CH_2C_6H_{13}} \\ \xrightarrow{CH_2=CHC_6H_{13}} \underset{(XVI)}{HOOCCHClCH_2CH(C_6H_{13})CH_2\dot{C}HC_6H_{13}} \quad , \end{cases}$$

$$(XVI) \xrightarrow{\circ\ 1,5\text{-}H} \underset{(XVII)}{HOOC\dot{C}ClCH_2CH(C_6H_{13})CH_2CH_2C_6H_{13}} \quad .$$

The scheme shows that, when the reaction is carried out in the presence of MNP, the formation of five spin-adducts corresponding to radicals (XIII)–(XVII), may be expected. The spin-adducts of radicals (XIV) and (XVI) as well as (XV) and (XVII) should not have different EPR spectra. Thus the problem reduces to the identification of three nitroxy-radicals:

$$\underset{(XVIII)}{HOOCCHCl{-}N(\dot{O}){-}C(CH_3)_3}, \quad \underset{(XIX)}{RCH_2CH(C_6H_{13}){-}N(\dot{O}){-}C(CH_3)_3} \quad ,$$

$$\underset{(XX)}{RCH_2CCl(COOH){-}N(\dot{O}){-}C(CH_3)_3} \quad .$$

The spectrum of radical (XVIII) is extremely complex and hinders the identification of other signals, overlapping them. However, special experiments showed that the stability of radical (XVIII) is very low, and its spectrum disappears almost immediately when irradiation ceases. It was therefore possible to identify the nitroxy-radicals (XIX) and (XX) by recording the spectrum several minutes after stopping irradiation.

In certain cases the spin-adducts have a very low stability and their EPR spectra cannot be recorded at all at room temperature. The study, mentioned previously, of the homolytic rearrangement of acetophenone diphenylmercaptal, occurring under the influence of ultraviolet irradiation, is of interest in this connection[74,75]. By carrying out this reaction in the presence of the MNP spin-trapping agent, it was possible to identify all the intermediate radicals in conformity with the scheme

$$C_6H_5C(SC_6H_5)_2CH_3 \longrightarrow \underset{(XXI)}{C_6H_5\dot{C}(SC_6H_5)CH_3} + \underset{(XXII)}{\dot{S}C_6H_5} \quad ,$$

$$(XXI) \xrightarrow{O_2} C_6H_5\underset{\underset{\textstyle O^{\cdot}}{|}}{C}(SC_6H_5)CH_3 \quad (XXIII) \quad ,$$

$$(XXIII) + C_6H_5C(SC_6H_5)_2CH_3 \longrightarrow \underset{(XXIV)}{C_6H_5C(SC_6H_5)_2\dot{C}H_2} \quad ,$$

$$(XXIV) \xrightarrow{\circ} \underset{(XXV)}{C_6H_5\dot{C}(SC_6H_5)CH_2SC_6H_5} \quad ,$$

$$(XXV) + DH^{\S} \longrightarrow C_6H_5CH(SC_6H_5)CH_2SC_6H_5 \quad .$$

---

‡The symbols 1,3-H and 1,5-H denote rearrangements involving 1,3- and 1,5-migrations of a hydrogen atom respectively.

§DH is a hydrogen donor.

At room temperature the EPR spectrum shows signals corresponding to the spin-adducts of radicals (**XXI**), (**XXII**), (**XXIV**), and (**XXV**). Only at a low temperature (between −65° and −50°C) was it possible to detect the spectrum of the spin-adduct of radical (**XXI**) (Table 7, No. 7) and hence elucidate the stage involving the initiation of this reaction.

Thus the method of spin-trapping agents has been used successfully recently to investigate a wide range of radical reactions of organochlorine and organosulphur compounds. The value of this method is particularly evident in those cases where the reactions proceed via several pathways, leading to a complex mixture of products. The identification of the intermediate radicals in these systems yields important information about the reaction mechanism, the role of individual stages, etc.

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The Mechanism of the Elimination of Ammonia in the Condensation of Primary Amino-compounds and Certain Syntheses of Nitrogen-containing Heterocycles

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Studies on the mechanism of the elimination of ammonia in the interaction of two amino(imino)-compounds or two amino-groups in the same compound, carried out using ^{15}N, are considered. Taking into account the difference between the properties of the amino-groups, several mechanisms, which explain the experimental findings, are proposed. The ideas developed have been used to interpret the mechanisms of reactions which have not been investigated by the ^{15}N isotopic method. The bibliography includes 70 references.

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I. INTRODUCTION

The reactions of amino-compounds with one another, accompanied by the elimination of ammonia, are very common in preparative and industrial practice and have therefore become important. These include the synthesis of secondary amines from primary amines, the synthesis of *N*-aryl- or *N*-alkyl-amides from unsubstituted amides and primary amines, the Fischer synthesis of indoles, the Bucherer or Borsche synthesis of carbazoles, and other reactions involving the formation of nitrogen-containing heterocycles. The determination of the pathways whereby nitrogen migrates in these processes constitutes a convenient and direct method for the elucidation of the relative reactivities of nitrogen atoms in the $-NH_2$, $=NH$, and NH_3^+ groups linked to various organic residues. The knowledge of the rules governing the variation of reactivity in series of amino-compounds is in its turn quite essential for the elucidation of the mechanisms of the corresponding processes and for the prediction of the pathways followed in new or hitherto uninvestigated reactions.

The study of the above reactions can also yield direct evidence for the relative reactivities of amino-groups. In other reactions of amines, such as, for example, solvolysis, interaction with aryl halides, acyl chlorides, etc., the mechanism of the process and its rate depend both on the nature of the amines and on the nature of the other reactant, so that the correlation between the rate constants and other parameters, on the one hand, and the properties of amines, on the other, frequently breaks down.

The pathways followed in the migration of nitrogen can naturally be elucidated only with the aid of the isotope technique. Isolated studies in this field began to be published from 1943 when concentrated ^{15}N preparations became available. Systematic research was carried out by the present author in 1954–1964 and by a group of German investigators in 1952–1967. The present author believes that the time has come to survey the results of all the studies carried out hitherto using heavy nitrogen and to describe the observed characteristics and mechanisms of the reactions. An attempt should also be made to use the results obtained with the aid of ^{15}N in order to elucidate the mechanisms of reactions which have not as yet been determined by the isotopic method.

II. CONDENSATION OF TWO AMINO-COMPOUNDS OR AMIDES

Reactions involving the condensation of two amines with elimination of ammonia have been known for more than 100 years. Nevertheless, the study of this process from the standpoint of the reactivity of the nitrogen atoms immediately poses a difficult problem: which nitrogen atom in the two amines is converted into ammonia? In certain cases a cautious prediction of the answer to this question can be made, as will be seen from the account below (for example, in the interaction of an amine with an amide). The general solution of this problem with the aid of the ^{15}N isotope can be achieved on the basis of the scheme

$$RNH_2 + R^1\overset{*}{N}H_2 \rightarrow RNHR^1 + \overset{*}{N}H_3 \quad .$$

One of the initial amines is prepared with an increased content of ^{15}N in the amino-group relative to the natural abundance (0.365% ^{15}N) and the site from which the amino-group is eliminated can be determined from the concentration of ^{15}N in ammonia and (or) the secondary amine. The results of isotopic analyses obtained in the first studies on the amine condensation reactions[1-4] are presented in Tables 1 and 2.

The uniform distribution of ^{15}N between the reaction products on condensation of labelled aniline hydrochloride with unlabelled aniline indicates rapid proton exchange between the anilinium ion and the aniline molecule via the mechanism

$$Ph\overset{*}{N}H_3^+ + PhNH_2 \rightleftharpoons Ph\overset{*}{N}H_2 + PhNH_3^+ \quad .$$

The ease of conversion of the arylammonium ion into an amine and conversely suggests that weakly basic amines can react under these conditions in the form of free bases. The catalytic role of the acid consists in facilitating proton transfer via the general mechanism of Brønsted acid–base catalysis[5].

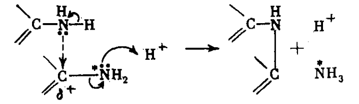
The results of the study of the condensation of [^{15}N]-benzamide with arylamines[1,2,6] are presented in Table 3. According to current ideas, ammonia is formed preferentially from the amide, which can be readily accounted for by the decrease of the basicity of the amide group NH_2 under the influence of the carbonyl group†.

Table 1. The condensation of primary amines in the presence of hydrochloric acid[1,2,6].

Starting substances				^{15}N content in reaction products, %	
labelled (% content of ^{15}N indicated in brackets)	$K_b \cdot 10^{10}$	unlabelled (0.37% ^{15}N)	$K_b \cdot 10^{10}$	secondary amine	NH_4Cl
Aniline (3.00)	3.82	Aniline	3.82	1.62	1.47
Aniline (2.15)	3.82	1-Naphthylamine	0.84	2.15	0.67
Aniline (9.3)	3.82	4-Aminophenol	66.0	9.0	0.46
1-Naphthylamine (9.3)	0.84	4-Aminophenol	66.0	3.25	5.35
1-Naphthylamine (8.4)	0.84	4-Chloroaniline	1.0	0.37	—
1-Naphthylamine (8.4)	0.84	3-Chloroaniline	0.3	0.40	—
Aniline (3.0)	3.82	n-Butylamine	$4 \cdot 10^6$	2.9	—

However, these studies firmly established that part of the amino-nitrogen is incorporated in *N*-arylbenzamide in reactions involving 1-naphthylamine and 9-aminophenanthrene; this unexpected result will be explained below.

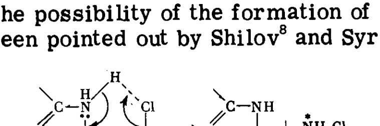
Since the essential feature of the condensation reaction involves the substitution of the amino-group by an aryl-amino-group, one can assume in principle that the reaction involves nucleophilic substitution:



(1)

The stronger base plays the role of the nucleophilic and adds to the positively charged carbon atom of the polarised C–N bond with the aid of the free electron pair of the nitrogen. On formation of the secondary amino-group, the previously more basic nitrogen atom loses a proton, which adds (evidently via the mediation of a catalyst) to the weakly basic amino-group, forming ammonia.

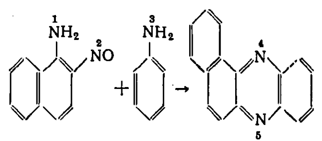
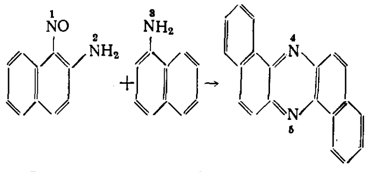
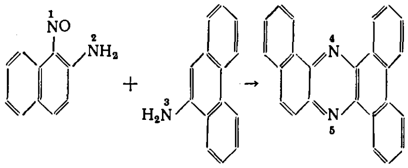
One cannot rule out the possibility that the reaction proceeds via an energetically favourable six-membered complex[7]; the possibility of the formation of such complexes has been pointed out by Shilov[8] and Syrkin[9]:



(2)

Comparison of the pathways leading to the elimination of amino-groups with the dissociation constants of the bases listed in Table 1 indicates the absence of a consistent relation between them. In the reaction of aniline with 1-naphthylamine the amino-group is split off from the weaker base, while in reactions of 3-chloroaniline with 1-naphthylamine or of aniline with n-butylamine it is split off from the stronger base; in the reaction of 4-chloroaniline with 1-naphthylamine, where the basicities of the two reactants are almost identical, the NH_2 group is split off wholly from only one component (1-naphthylamine), while in the condensation of nitrosonaphthylamine with 1-naphthylamine (Table 2) and of benzamide with polycyclic amines (Table 3), it is split off from both components. Nevertheless the mechanism described by Eqns. (1) and (2) provides for the elimination of the less basic amino-group. All the data obtained cannot therefore be accounted for by the S_N2 mechanism [described by Eqns. (1) and (2)] and, while remaining fundamentally correct, it needs to be revised. We may recall that the NH_2 groups attached to alkyl, aryl, or acyl residues differ sharply in their properties. Their basicity also varies within the limits of the same class of compounds as a function of the substituents, an increase of the number of benzene rings, steric hindrance, and other factors.

Table 2. Condensation of nitrosonaphthylamines with aromatic amines[3,4].

No. of expt.	^{15}N content, %				
	N (10)	N (2)	N (3)	N (4)*	N (5)*
					
1	0.37	0.37	8.6	8.4	0.37
2	0.37	8.7	0.37	0.37	8.6
					
3	0.37	0.37	8.6	0.37	5.5
					
4	0.37	8.7	0.37	0.37	8.6
5	10.1	0.37	0.37	9.9	0.37

*The ^{15}N content among the $N_{(4)}$ and $N_{(5)}$ atoms in the products was determined from the average ^{15}N concentration in both positions (by analysis) and the 0.37% content at one of them (known from the experimental conditions).

Taking into account these relations, one may suggest that there should be several mechanisms of the interaction of amino-compounds with one another. In the aromatic series, where the difference between the basicities of the amines are in most cases small, the possibility of the

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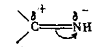
† The elimination of the amide nitrogen of urea has been demonstrated using ^{15}N in well known studies on the synthesis of uric acid by the condensation of urea with uramil[20] or diaminouracil[20,21].

formation of quinonoid structures plays a significant role. In the instances investigated by the present author, where 1-naphthylamine always loses its amino-group on condensation with an amine of the benzene series (except 4-aminophenol which requires separate consideration), the monocyclic amine reacts with the quinonoid form of 1-naphthylamine. The basicity of the latter is suppressed and the reactive group



is subjected to nucleophilic attack by the NH_2 group:

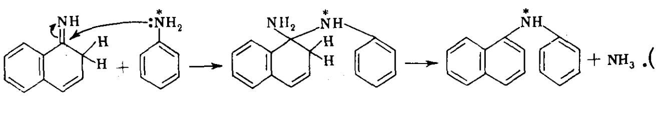
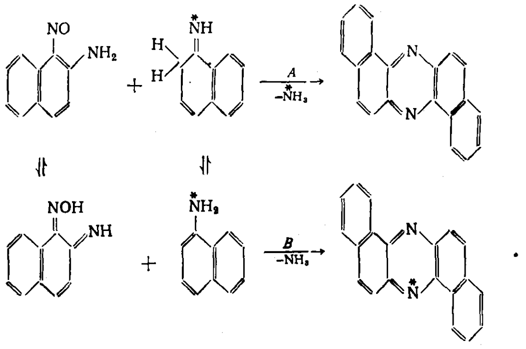

(3)

Table 3. Condensation of $[^{15}N]$-benzamide with amines[1,2,6].

Amines	^{15}N content, %			Amount of benzamide nitrogen in N-aryl-benzamide, %
	in initial benzamide	in N-aryl-benzamide	in NH_4Cl	
Aniline	2.15	0.51	2.07	~0
4-Aminophenol	9.30	0.44	—	~0
1-Naphthylamine	8.16	0.77	7.25	5
9-Aminopenanthrene	8.75	2.1	5.7	21

When 1-naphthylamine condenses with 1-nitroso-2-naphthylamine, the stabilities of the quinonoid structures are approximately the same, which leads to the loss of nitrogen by both components (the nitroso-group is not split off; see Table 2). The reaction mechanism may be represented by the scheme



The results of isotopic analysis[3,4] showed that the contributions of pathways *A* and *B* are 38% and 62% respectively. This can be explained by the fact that the formation of the quinonoid form from nitrosonaphthylamine may be facilitated by the conjugation of the amino-group with the N=O group. Among the amines investigated by the present author, 9-aminophenanthrene shows the greatest tendency towards the formation of quinonoid structures. In the interaction with 1-nitroso-2-naphthylamine (Table 2) it therefore always reacts as the quinone imine and its amino-group is lost completely.

The condensation of aniline with n-butylamine[2] (which is 10^6 times stronger as a base) is accompanied by the elimination of the more basic amino-group only, in complete conflict with the mechanism involving reactions (1) and (2). One must suppose that the following reaction occurs in this instance:

$$PhNH_2 + Bu\overset{*}{N}H_2 \xrightarrow{H^+} Ph\ddot{N}H_2 + H_3\overset{*}{\underset{+}{N}}-CH_2-(CH_2)_2CH_3 \longrightarrow$$

$$\longrightarrow Ph-NH-Bu + \overset{*}{N}H_4^+ \quad . \qquad (4)$$

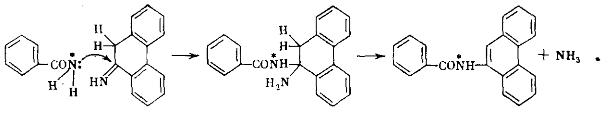
The very strong base therefore exists mainly as the alkylammonium ion, which is subjected to nucleophilic attack by the aromatic amine. Mechanism (4) must undoubtedly occupy an important place among amine condensation reactions, since these processes usually occur in the presence of acid catalysts. As will be shown below, the involvement of amines as ammonium ions can be postulated also in the interaction of amines with not quite so greatly different basicities and also in the cyclisation of the intermediate complexes containing two amino- or imino-groups.

The reactions with participation of 4-aminophenol may occur mainly (with aniline) or partly (with 1-naphthylamine) via mechanism (4), since 4-aminophenol is 17 times more basic than aniline. Furthermore, there exists a hydrolytic mechanism with preliminary formation of hydroquinone. This reaction pathway has been demonstrated experimentally[2].

The main pathway in the condensation of an amine with an amide is determined by the mechanism of the nucleophilic substitution at the carbonyl carbon atom, which is positively charged owing to the polarisation of the C=O group. An analogous mechanism has been adopted for the acylation or nitrosation of amines[10] and for the addition of nucleophiles to sulphonamides[11]. The same mechanism has also been proposed for the reaction of hydrazine with monoarylurea[12] and for the transamination of *N*-arylacetamides[13]. It may be that the condensation proceeds via a six-membered cyclic complex [see Scheme (2)]. A similar complex has been proposed by Syrkin and Moiseev[14] to account for the hydrolysis of benzamide in an acid medium. The role of the acid catalyst is to enhance the positive charge of the carbonyl carbon atom as a result of the protonation of the oxygen atom.

The second reaction pathway, leading to the elimination of amino-nitrogen, involves the participation of 9-aminophenanthrene or 1-naphthylamine in the quinonoid form and of benzamide as the nucleophile. The mechanism of this reaction can be represented by Scheme (5) below.

The results obtained in the condensation of amines with amides have shown that, in a system containing several benzene rings, the delocalisation of the electron density of the free electron pair of nitrogen and the concomitant formation of an imine may compete with the analogous phenomena in benzamide.


(5)

Further investigations[15-18] provided new evidence confirming the above mechanisms. Table 4 compiles the results obtained in these studies. They also show that, on condensation with both stronger and weaker amines of the benzene series, 1-naphthylamine usually loses its amino-group, but retains it on interaction with 9-aminoanthracene. Such behaviour of amines is fully consistent with the mechanism represented by Scheme (3), according to which the ability to split off NH_2 groups is determined by the stability of the quinoid structures and increases in the sequence: monocyclic amine < dicyclic amine < tricyclic amine.

Table 4. Condensation of two amino-compounds[15-19].

Labelled component	Amine of benzene series	pK_b	Amount of nitrogen from the amine of the benzene series in the secondary amine formed, %
1-Naphthylamine (pK_b = 10.04)	*o*-Toluidine	9.48	100
	Aniline	9.35	100
	m-Toluidine	9.20	100
	p-Ethylaniline	–	99
	p-Toluidine	8.84	86.5
	p-t-Butylaniline	9.05	70
	p-Phenetidine	8.80	68
	2,4-Dimethylaniline	9.15	57
	p-Anisidine	8.56	32
	p-Phenylenediamine	7.92	20
	p-Aminoacetophenone	–	100
	p-Fluoroaniline	9.35	100
	p-Chloroaniline	9.93	100
	m-Chloroaniline	10.48	100
	m-Bromoaniline	10.42	100
	m-Iodoaniline	10.39	100
	9-Aminoanthracene	–	0
8-Aminoquinoline (pK_b = 10.01)	Aniline	9.35	81*
	p-Toluidine	8.84	95*
	p-Phenetidine	8.80	75*
	p-Anisidine	8.56	61*
5-Aminoquinoline	*p*-Toluidine	8.84	41*
	p-Phenetidine	8.80	35*

* Calculated by the present author from experimental literature data[17] (an incorrect calculation is quoted in the relevant paper[17]).

In many reactions (see Table 4) labelled nitrogen was found to be distributed within the reaction products—the secondary amine and ammonia[15-17]. Having noted that in these instances an amine more basic by 1–2 orders of magnitude reacts with 1-naphthylamine, one may assume that the former is partly converted into an $ArNH_3^+$ salt and then interacts via mechanism (4). Thus mechanisms (3) and (4) compete in this instance. The second reaction pathway should naturally be associated with the proton-accepting properties of the stronger base. Indeed the authors found that the degree of elimination of the imino-group is satisfactorily correlated with the dissociation constant of the amine of the benzene series and the Hammett σ constant of the substituent in the benzene ring. Individual straight lines were obtained for condensation with 1-naphthylamine, 8-aminoquinoline, and 5-aminoquinoline.

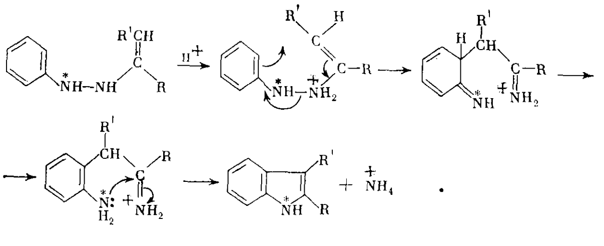
In the experiments on the condensation of urea with aniline and methylamine hydrochlorides an unexpected result was obtained—the elimination of the urea nitrogen[15]. The mechanism of the interesting reaction between urea and acetamide may be treated only qualitatively in the sense that ammonia is eliminated from both amides. The degrees of involvement of urea and acetamide nitrogen in the formation of acetylurea cannot be calculated from the analytical determination of ammonia (as was done by Krumbiegel and Hübner[15]), because the latter is obtained also from urea via a side reaction involving the formation of biuret.

Summarising the findings described above, one may say that mechanisms (1), (2), (3), (4), and (5),[1,2,6,7] as well as substitution at the carbonyl carbon atom of the amide[10], acting independently or competing with one another, can explain all the results obtained hitherto for the condensation of amines. The basicity of amines is correlated with the degree of elimination of the amino-group within narrow limits of pK_b values for reactions of similar amines with the same reactant (the second amino-compound)[19].

III. SYNTHESES OF HETEROCYCLIC COMPOUNDS

In certain syntheses of heterocycles from nitrogen-containing substances intermediates or short-lived complexes are formed in which there are at least two amino-groups. In most cases these reactions are complex, comprise many stages, and different aspects of their mechanisms may be discussed. Here they will be considered from only one standpoint—which amino-group is eliminated on cyclisation (in the form of ammonia) and the mechanism of such elimination.

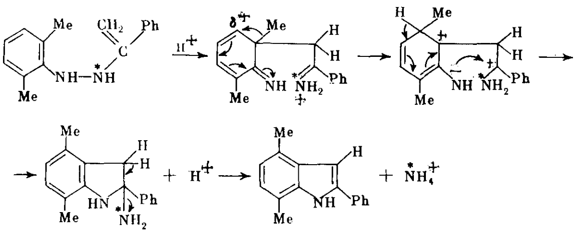
The situation described is encountered in numerous Fischer syntheses of indole and carbazole derivatives from aldehyde or ketone arylhydrazones. It has been established with the aid of ^{15}N that, in the cyclisation of acetophenone[22] and acetone[23] phenylhydrazones, the amino-group attached to the aliphatic end of the intermediate diamine is eliminated, while the much less basic aromatic amino-group enters into the indole ring. This result can be readily explained by the mechanism developed on the basis of numerous studies[24,25], according to which the more basic $-NH_2$ (or $=NH$) group is protonated by the acid. This induces a positive charge on the carbon atom adjoining the nitrogen atom and the former is subjected to nucleophilic attack by the aromatic amino-group:


(6)

A special case of reaction (4), in which two amines with markedly different acid properties interact, may be seen in mechanism (6). The mechanism is in principle unaffected by the fact that two amino-groups in the intermediate complex (compound) interact rather than two different amines.

The migration of nitrogen in accordance with mechanism (6) has been confirmed by subsequent investigations. A study of the reductive contraction of the [2-^{15}N]-4-phenylcinnoline ring showed that the formation of the indole derivative is accompanied by the elimination of the aliphatic amino-group[26]. Suvorov et al.[27] cyclised acetaldehyde phenylhydrazone in order to obtain an indole labelled with ^{15}N, free from substituents in the pyrrole ring. Having labelled the nitrogen in the 1-position in the first experiment and that in the 2-position of phenylhydrazine in the second, they obtained results agreeing with elimination of the aliphatic amino-group from the intermediate diamine. A study of the reaction of acetophenone 2,6-dimethylphenylhydrazone also revealed the elimination of the amino-group from the aliphatic end of the intermediate complex[28]. In clear conflict with mechanism (6), the authors[28] present a mechanism where the less basic amino-group (aromatic amino-group and even the NH group of the secondary amine) is protonated twice.

The present author suggests that this mechanism is erroneous, particularly since a result consistent with experiment is obtained via mechanism (7), postulated here with correct allowance for the relative basicities. Results which can be explained by mechanism (4) have been obtained[29] in a study of the cyclisation of cyclohexanone phenylhydrazone. The 10.1% excess of ^{15}N among the nitrogen atoms in the 1-position of phenylhydrazine was fully incorporated in tetrahydrocarbazole [Scheme (8)].



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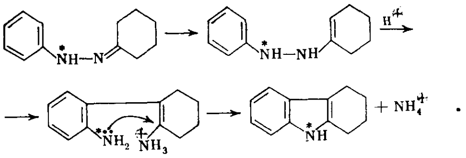
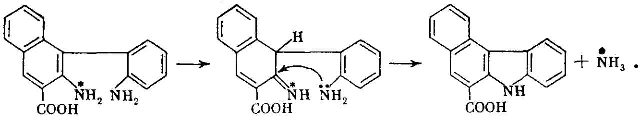


(8)

Analogous reactions involving aromatic compounds lead to carbazole derivatives. Clusius and Barsh[30] investigated one such reaction—the formation of benzocarbazole-carboxylic acid from 2,3-hydroxynaphthoic acid and phenylhydrazine labelled with ^{15}N. The main reaction pathway (the contribution of which amounts to 88.5%) involves the elimination of the amino-group from the naphthalene ring [Scheme (9)]‡. It is easily seen that mechanism (6) is unsuitable in this instance; it requires the elimination of the more basic amino-group from the benzene ring, which conflicts with experimental findings.

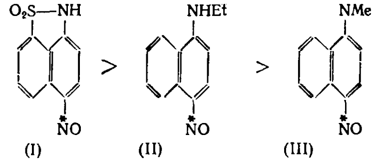
In order to account for these results, the present author suggests a mechanism of type (3), according to which the intermediate reacts as an iminoamine with a quinonoid structure of the naphthalene ring [Scheme (9)]. Cyclisation of this diamine leads to a carbazole derivative which does not contain ^{15}N, in agreement with experiment.



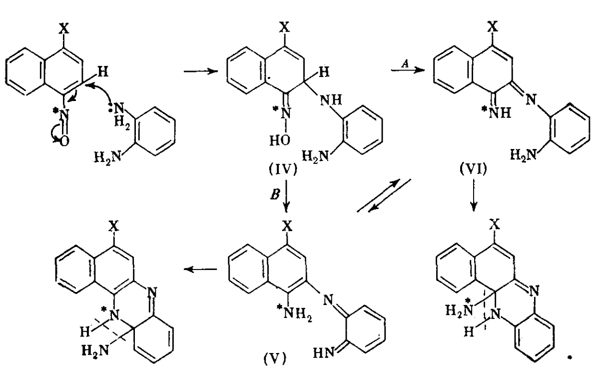
(9)

Holt and McNae[31] investigated the mechanisms of the interaction of [2-^{15}N]-phenylhydrazine with 2-naphthol. A small proportion of ^{15}N (~0.5%) was incorporated in the benzocarbazole formed under these conditions. It was shown that the labelled and unlabelled benzocarbazoles are formed by different reactions. The intermediate formation of the [2-^{15}N]-phenylhydrazone of 1,1-dihydro-2-oxonaphthalene followed by stages analogous to those in the Fischer synthesis of indole was postulated. The mechanism proposed for the main reaction pathway—the formation of unlabelled benzocarbazole with participation of the protonated "benzene" NH_2^- group—is unsuitable, because it would lead to the elimination of this group, which conflicts with the experimental results. The present author suggests that the main reaction proceeds via an intermediate diamine with participation of the quinonoid structure of 2-aminonaphthalene, by analogy with Scheme (9). The side reaction (its contribution is approximately 5%), leading to labelled benzocarbazole, evidently proceeds via the *ortho*-semidine rearrangement of the hydrazone. Other versions of the incorporation of ^{15}N into benzocarbazole proposed by the author[31] are erroneous, because they conflict with isotopic data for similar reactions.

The synthesis of phenazine derivatives from aromatic nitroso-compounds and *o*-phenylenediamine is accompanied by the evolution of ammonia. In the study of the pathway followed in the migration of nitrogen in such reactions it was found[32] that the nitroso-group labelled with ^{15}N is almost completely eliminated in the form of ammonia from the nitrosonaphthosultam (I), to the extent of 55% from *N*-ethyl-4-nitroso-1-naphthylamine (II), and to the extent of 23% from *NN*-dimethyl-4-nitroso-1-naphthylamine (III). The remainder of the ^{15}N is incorporated in the phenazine derivative.



Scheme (10) was proposed to account for these results. The intermediate complex (IV) formed initially may be subsequently converted into compounds (V) and (VI), which are in equilibrium. This leads to the elimination of different imino-groups, with and without ^{15}N, which results in the distribution of heavy nitrogen among the reaction products.



(10)

The position of the (V) ⇌ (VI) equilibrium is determined by the nature of the substituent X. The sultam group has electron-accepting properties and promotes the formation of complex (VI), from which ^{15}N is eliminated; the contribution of the reaction via pathway *B* is insignificant—not more than 3% (which may even be due to experimental

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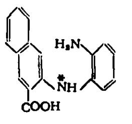
‡The side reaction involving the incorporation of ^{15}N in benzocarbazolecarboxylic acid proceeds to the extent of 11.5% (determined from its isotopic analysis) or to the extent of approximately 5% (found by the analytical determination of ammonia). The authors postulate the *ortho*-semidine rearrangement with formation of the intermediate



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error). The introduction of an electron-donating substituent stabilises complex (V) and increases the basicity of the amino-group attached to the naphthelene ring; the reaction with the nitrosoamine (II) therefore proceeds to the extent of 50% via pathway *B*. The substituent with still more marked electron-donating properties in compound (III) promotes a further increase of the contribution of pathway *B*, which predominates in this instance.

IV. REACTION MECHANISMS

Examination of the literature data and the experimental studies described here lead to the conclusion that the dissociation constants of the bases do not always determine the mode of dissociation of the C–N bond in nucleophilic condensation reactions between two amines. The correspondence between the rate constants and the pK_b values for the amines breaks down also for other nucleophilic substitution reactions. For example, the rate of the reaction of 1-chloro-2,4-dinitrobenzene with chloroanilines and 1-naphthylamine decreases in a series which is not related to the variation of the basicity of the amines[32]:

	p-Chloroaniline	*m*-Chloroaniline	1-Naphthylamine
$k_{45°}$	$2{,}8 \cdot 10^{-3}$	$0{,}86 \cdot 10^{-3}$	$0{,}36 \cdot 10^{-3}$
pK_b	10,0	10,52	10,04

The first stage of the interaction between the two amines [Scheme (1)] involves attack by the nitrogen atom of the nucleophilic component on the positively charged carbon atom of the second amine. This stage should therefore be promoted by a higher electronic charge density at the nitrogen atom and a positive charge on the carbon atom. Sixma[33] used the energy of the localisation of the free electron pair at the nitrogen atom as the criterion of nucleophilic reactivity. It has been shown[34] that the electronic charge is greater the lower the localisation energy. In the reactions of a series of polycyclic amines with 1-chloro-2,4-dinitrobenzene, Sixma found that the logarithms of the rate constants for the reactions vary linearly with the charge on the nitrogen§, provided that steric factors do not interfere.

The dissociation constants of the bases may also be to some extent proportional to the electronic charge on the nitrogen atom. For example, an approximately linear relation has been found between pK_a and the electronic charge q_N for a series of methylbenzacridines[35]. However, the correspondence between pK_a and q_N breaks down to a large extent for many bases with different molecular skeletons (Table 5).

The first stage of reaction (1) is promoted by electron-accepting substituents as well as other factors intensifying the positive charge on the carbon atom of the electrophilic molecule and ultimately increasing the amount of double-bond character of the C–N linkage. The increase of the C–N bond order leads ultimately to the formation of a quinonoid structure. Compounds with quinonoid structures show a greater tendency towards nucleophilic substitution reactions. Bunnett and Zahler[36] believe that this problem is still obscure, but quote evidence in support of the latter assertion. Thus halogenonitrobenzenes have a higher C–N bond order and react very readily with nucleophiles. It is also known that quinoneimines are more readily hydrolysed than amines. Thus, amino-compounds which readily give rise to quinonoid forms should combine with a nucleophile more readily, eliminating their amino-group at the same time. Presumably in the reaction of two aromatic amines the electrophile is the compound whose quinonoid form is more stable and which has a higher conjugation energy. It has been found experimentally that the degree of elimination of the amino-group increases in the sequence aniline < 1-naphthylamine < 9-aminophenanthrene[1,2]. This series has been compared (Table 6) with the electronic charges on the nitrogen atom q_N (calculated by the Slater–Pauling method[37]), the charges on the exocyclic carbon atom of the hydrocarbon analogue of the amine q_C, and the C–N bond orders[33]. Table 6 also shows that the oxidising potential of the corresponding quinone decreases, i.e. the stability of the quinonoid form increases, in the direction in which the ability of the amine to split off the amino-group increases[38].

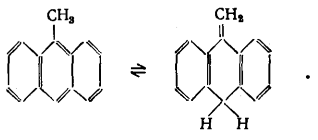
Table 5. Relation between the electronic charge on the nitrogen (q_N) and pK_a for the base[35].

Compound	q_N	pK_a
Pyridine	1,190	5,23
Isoquinoline	1,202	5,33
1-Aza-anthracene	1,205	5,05
Quinoline	1,221	4,91
Acridine	1,227	5,60

Table 6. Comparison of the reactivities of aromatic amines with the charges on the nitrogen (q_N), the charges on the exocyclic carbon atom (q_C), the bond orders P_{CN}, and the oxidation potentials of quinones (E).[7]

Parameter	Aniline	1-Naphthyl-amine	9-Amino-phenan-threne
q_N	1,841	1,817	—
q_C	0,571	0,450	0.446
P_{CN}	1,160	1,180	—
E, b	0.794	0,576	0.460

The increase of the ability to form quinonoid structures with increase of the number of benzene rings also follows from the benzenoid–quinonoid tautomerism of methyl derivatives or aromatic hydrocarbons. Thus, whereas 9-methylanthracene exists mainly in the benzenoid form [Scheme (11)], the quinonoid form predominates in methylpentacene. According to Syrkin and Dyatkina[39], this behaviour is caused by the increase of the π-electron energy of the quinonoid tautomer with increase of the number of rings:



(11)

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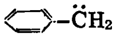
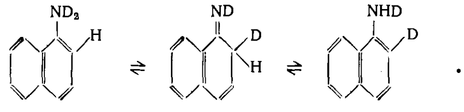
§ For simplicity, the charge on the exocyclic carbon atom in the hydrocarbon analogue of the amine  was calculated.

The formation of the quinonoid forms of polycyclic amines might serve as a convenient pathway for the migration of protons of the amino-groups to the ring and conversely. Such exchange has been investigated using deuterium introduced into the amino-group[40]. No exchange involving aniline was observed in a neutral medium, but it occurred at an appreciable rate at 180–200°C in the 2- and 4-positions of 1-naphthylamine. Since the rate of exchange was independent of the concentration of amine in the tetralin solution, the following intramolecular mechanism involving an intermediate quinonoid structure was proposed for the exchange:



(12)

This process could also proceed via a π-complex¶. An increase of electron density in the 2- and 4-positions promotes the addition of the amine proton in these positions with formations of a quinonoid tautomer†.

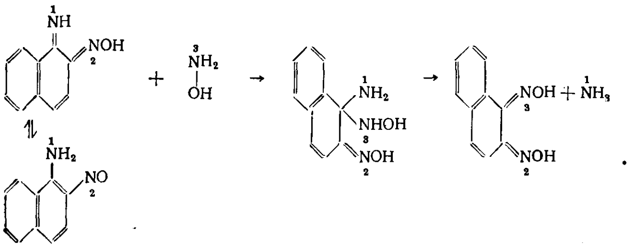
The foregoing discussion permits the conclusion that the benzenoid-quinonoid tautomerism in the reactions of polycyclic aromatic amines plays an important role. Here it was demonstrated in relation to the interaction of two amines, but there is no doubt that the conclusion is of more general validity.

The acid–base properties of amines also play a significant role in determining the mode of dissociation of the C–N bonds in the reactions under consideration. As we have seen quantitative relations have been observed in specific instances[19] between the reactivities of the amines, the pK_b values, and the Hammett σ constants. In elucidating the mechanism of the elimination of ammonia one must therefore take into account the relative basicities of the reacting amino-groups.

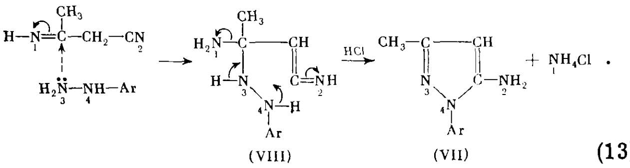
V. INTERPRETATION OF THE MECHANISMS OF PROCESSES WHICH HAVE NOT BEEN INVESTIGATED USING ^{15}N

In this section an attempt will be made to apply the ideas developed above for the mechanism of the condensation of amines to analogous reactions in which the nitrogen migration pathways have not been established by isotopic methods using ^{15}N.

2-Nitroso-1-naphthylamine reacts with hydroxylamine to form 1,2-naphthoquinone dioxime[43]. The mechanism of this reaction can be represented as follows:



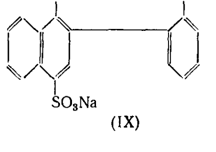
The reaction of diacetonitrile with arylhydrazines in the presence of hydrochloric acid[44] leads to 5-amino-1-aryl-3-methylpyrazoles (VII), which are used as the nitrogen-containing components in the synthesis of dyes. It appears that the arylhydrazine nitrogen atoms attack the carbon atoms of the nitrile and imino-groups to form $N_{(3)}$–C and $N_{(4)}$–C bonds. An intermediate complex (VIII) should be formed in the initial stage and ammonia containing the nitrogen atom of the imino-groups of the diacetonitrile is eliminated from it [Scheme (13)]. The polarisation of the $N_{(1)}$–C bond promotes the protonation of the $N_{(1)}$ atom by the acid present.



(13)

When phenylhydrazine reacts with aminonaphthalene or naphthols, the products are hydrazo-compounds, which are converted into carbazole derivatives in the presence of acid[45]. In particular, the reaction of phenylhydrazine with 4-, 5-, 6-,[46] and 7-sulphonic acid of 1-naphthylamine[47] in the presence of sodium bisulphite yielded the corresponding benzocarbazolesulphonic acids. The hydrazo-compound detected in these studies is obtained by the nucleophilic substitution of the "naphthalene" amino-group by the phenylhydrazyl residue. The reaction is favoured by the tendency of the substituted naphthylamine to form a quinonoid structure containing the HN=C< group. This mechanism explains why such reactions proceed with bicyclic and tricyclic amines but not with amines of the benzene series: the conjugation of the free electron pair of the nitrogen with the π electrons of the ring, which largely determines the capacity for the formation of the quinonoid form, is insufficient for this purpose in the benzene series.

According to isotopic data, the cyclisation of the intermediate diamine (IX), which has also been detected in the reaction medium[46], should proceed in reactions of this kind[2 3 16 31] with elimination of the amino-group from the naphthalene ring:



(IX)

The elimination of the "benzene" NH₂ group, which can be achieved, for example, by the *ortho*-semidine rearrangement of the hydrazo-derivative, is in this case still less likely than in the cyclisation of the [2-^{15}N]-phenylhydrazone of 1,1-dihydro-2-oxonaphthalene[31] owing to the presence of the sulpho-group. To demonstrate the occurrence of the side reaction (its contribution is probably less than 5%), an experimental test using ^{15}N is required.

The mechanism of the Fischer synthesis of indole derivatives from the phenylhydrazones of aliphatic or alicyclic ketones and aldehydes has been fairly clearly established (as a result of numerous studies, mainly those of Robinson's school). In the last stage of this mechanism ammonia is eliminated solely from the aliphatic component of the intermediate diamine. It has been shown[24, 31] that the

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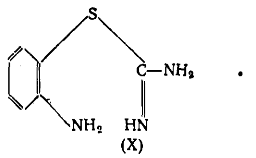
¶ An intramolecular mechanism involving π-complexes has been proposed for proton exchange involving toluidine hydrochloride in the solid phase[41].

† The four versions of the bimolecular mechanism proposed[42] for the self-exchange in aromatic amines do not conflict with these conclusions, because they refer to proton exchange in the presence of the alkaline catalyst PhNDK.

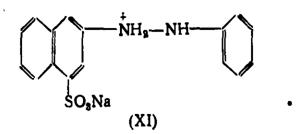
protonation of the aliphatic amino-group plays an important role in the elimination of ammonia. This mechanism is invoked in many investigations of the Fischer synthesis of indole derivatives[48,49]. In certain studies cyclisation mechanisms without protonation but with conversion of the aliphatic amino-group into an imino-group, for example, with formation of structure (X), [50-52] has been suggested:



(X)

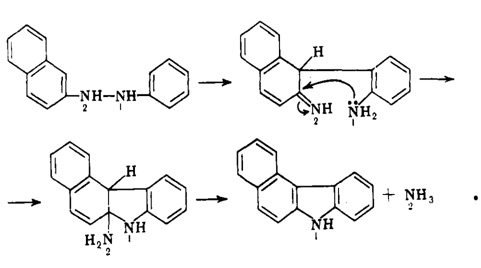
This mechanism should lead to the same ammonia elimination pathway, but it is in essence not unambiguous, because the aromatic amino-group can also be converted in certain cases into an imino-group and this would lead to its elimination in the form of ammonia, which conflicts with isotopic data.

Drawing an analogy between the Bucherer and Fischer syntheses, Seeboth[53] proposed a mechanism with the intermediate structure (XI):



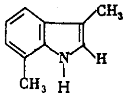
(XI)

The mechanism involving this structure, where the less basic nitrogen atom is protonated, appears to be doubtful. An analogous mechanism has been suggested in a paper[54] dealing specifically with the Bucherer reaction. Furthermore the Bucherer synthesis of benzocarbazole can be described by mechanism (14) with participation of the quinonoid form of naphthalene. The acid, which promotes the elimination of ammonia, catalyses the process via the general mechanism of acid catalysis:

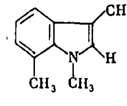


(14)

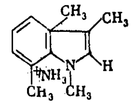
Mechanisms consistent with isotopic data are usually suggested in the literature for the interpretation of the Fischer syntheses of indoles and carbazoles, i.e. it is postulated that the amino-group attached to the aliphatic (or alicyclic) part of the molecule is always eliminated from the intermediate diamine (or dienoneimine). Only in two papers by the same workers[55,66] are mechanisms proposed in which the aromatic amino-group is eliminated to an equal extent. In these studies the interaction of *N*′-methyl-2,6-dimethylphenylhydrazine with propanal, 2-methylpropanal, and 2-methylcyclohexanone was investigated. Thus the reaction with propanal yielded a substance with structure (XIII) in addition to the normal indole (XII):



(XII)

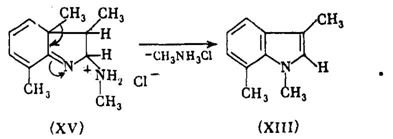


(XIII)



(XIV)

To explain this, the authors postulate a side reaction involving the formation of the intermediate (XIV) from which compound (XIII) is obtained by the elimination of the aromatic amino-group. Apart from the fact that this mechanism conflicts with all isotopic data for reactions of this kind, it is by no means necessary for the explanation of the experimental data presented. Product (XIII) can be obtained from the intermediate (XV), the formation of which via mechanism (15) in the course of the normal Fischer synthesis was confirmed by the above authors themselves with the aid of ^{1}H NMR. The methyl group migrates from the benzene ring to the nitrogen atom and the quinonoid structure is converted into the more stable benzenoid structure:



(15)

The interaction of amines with amides proceeds more readily than the reaction between two amines. Aniline reacts with urea at 160°C even in the absence of acids, forming diphenylurea[57]. Davis and Underwood[58] found a general method for the preparation of symmetrical diarylureas involving the heating of urea with primary aromatic amines. The mechanism of this reaction with aliphatic and aromatic amines of the benzene series gives rise to no doubts and evidently reduces to the elimination of the amide group. This can also be said of the reactions of mesidine with urea and of mesitylurea with hydrazine[12] as well as reactions of glycine and ethylglycine with urea[59] and of 2- and 3-aminopyridines with urea[60]. However, categorical predictions should not be made for the interaction of urea with 6-aminoquinoline[60], since, according to the present author's data[6], the dicyclic amine can lose part of its amino-nitrogen on reaction with an amide.

The reactions between an arylurea and an arenesulphonamide has been described[61]. One of the amides plays the role of the nucleophile:

$$RSO_2NH_2 + R'NHCONH_2 \rightarrow RSO_2NHCONHR' + NH_3 \quad .$$

The site from which the aminogroup is eliminated may be determined only by introducing ^{15}N into one of them. Admittedly one may assume that the withdrawal of electron density from the nitrogen atom in the sulphonamide is more pronounced than the corresponding effect in urea and the latter therefore retains its nitrogen atoms.

In transamination reactions amines displace one another from secondary amines, *N*-arylamides, and other complex compounds. Since transamination is associated with the competition between the reactivities of the interacting amines, it is of interest to examine these amines.

Stavrovskaya[62] investigated the transamination of benzyldiethylamine with various aromatic amines in hydrochloric acid:

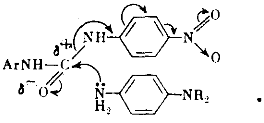
$$PhCH_2N(C_2H_5)_2 + ArNH_2 \xrightarrow{HCl} PhCH_2NHAr + NH(C_2H_5)_2 \quad .$$

Although the K_b values for the aromatic amines investigated varied in the range $(4-2000) \times 10^{-12}$, the yields of arylbenzylamines changed little (20–35%). The cause of this should be sought in the fact that all these weak amines displace diethylamine, which is a stronger base by 5–6 orders of magnitude. Evidently this possibility arises due to the presence of the acid, which converts the initial tertiary amines into the electrophilic ammonium ion. The low yields of the transamination product can be explained by the reversibility of the process and the more marked nucleophilic properties of diethylamine. A similar transamination involving n-aminobenzyldiethylamine was observed in another study[63].

Many instances of transamination have been observed in the series of urea derivatives. In the study already quoted[58] mention is made of the reaction of the symmetrical dimethylurea with aniline, which leads to the formation of diphenyl- and partly ethylphenyl-urea. Gerchuk et al.[64] carried out an extensive study of transamination in the series of substituted ureas. The results, which the present author compared with the basicities of the amines, permit the conclusion that the equilibrium in reaction (16) has shifted towards the displacement of the less basic amine. The authors propose a mechanism involving the preliminary decomposition of the arylurea to an aryl isocyanate, which reacts more readily with the stronger bases:

$$\text{ArNHCONHAr} + 2\text{Ar'NH}_2 \rightleftharpoons \text{Ar'NHCONHAr'} + 2\text{ArNH}_2 \quad . \qquad (16)$$

The same view is held by Kutepov and Potashnik[65], who investigated the interaction of bis(trichlorophenyl)ureas with aniline. However, this mechanism conflicts with the stability of arylureas, which has been pointed out by Heintz[59]. One may add that this type of exchange of amines has been found in the series of entirely stable *N*-arylacetamides. One must therefore assume that transamination takes place (see also Kogan and Kutepov[66]) via a nucleophilic substitution reaction, evidently involving an S_N2 mechanism. The redistribution of electron density in the intermediate complex (XVI) promotes the elimination of the weaker base.

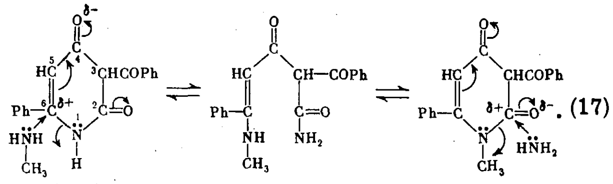


(XVI)

Transamination involving *N*-arylacetamides[13] takes place under very severe conditions (260°C, 100 atm, 2–5 days). The reaction of acetylpentylamine takes place more readily with aliphatic amines than with aniline. Primary amines also react more vigorously. The reactivity of amines in this process increases greatly as the phenyl groups become more remote, which can be seen from the following sequence:

aniline ≪ benzylamine < β-phenylethylamines.

The reactivity of the amino-groups is not correlated with their basicity. The authors therefore attribute much importance to steric hindrance. The mechanism of the transamination reaction is treated as a reversible nucleophilic substitution reaction; this conclusion has also been confirmed by other data[67]. Ridel' and Gerchuk[68] found that transamination takes place much more readily in the presence of hydrochloric acid, which can be accounted for by the induction of a positive charge on the carbonyl carbon atom on protonation. Like Porai-Koshits[69], they found that the strong base is displaced by the weak one. In certain cases this can be explained by the great excess (by a factor of 15–20) of the weaker base.



(XVII) (XVIII) (17)

The exchange of amines has been observed by Petrenko-Kritchenko and Shettle[70] when the "ammonia derivative of dehydrobenzoylacetic acid" (XVII) was acted upon by methylamine or aniline: there is a reversible exchange of the R–N< residues, where R = H, Me, or Ph. The present author suggests that this exchange begins with the addition of the amine to the $C_{(2)}$ or $C_{(6)}$ atom [Scheme (17)]. After ring opening, the intermediate aminoamide (XVIII) is formed‡ and this can again cyclise, regenerating the starting substances or giving rise to substitution products, which can be accounted for by the reversibility of this reaction.

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‡ When the $C_{(2)}$ carbon atom is attacked by methylamine, the intermediate aminoamide has a different structure, but the nature of the reaction remains unaltered.

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Natural and Synthetic Acetylenic Antimycotics

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The available information about natural and synthetic acetylenic compounds exhibiting antifungal activity is surveyed and it is shown that the class of acetylenic compounds with functional groups is extremely promising as regards the search for new drugs, particularly in view of the increase of the number of strains which have acquired immunity to the preparations used at the present time.

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I. INTRODUCTION

Fungal diseases (mycoses) affect man, various animals, and plants. Agents responsible for mycoses are numerous and the clinical symptoms are various[1-6]. Fungal diseases of the skin, caused by parasitic fungi or dermatomycetes, are encountered in all regions of the world. Humanity has suffered from mycoses since ancient times. They are highly contagious and give rise to chronic conditions. Clinical observations have shown that dermatophytes, which have become adapted by evolution to the skin and its derivatives, can sometimes affect also internal organs, bone tissue, and the central nervous system[5-7]. Although skin mycoses affect mainly the surface layers of the skin, they constitute a serious problem for the health service since the incidence of certain skin mycoses is comparable to that of the common cold or dental caries and the treatment of patients with skin mycoses is enormously expensive[4-5]. The problem of the chemotherapy of patients with fungal inflections has attracted the attention of a wide range of specialists-dermatologists, pharmacologists, biochemists, and chemists[6-10].

Antifungal antibiotics (griseofulvin, nystatin, and others) have occupied a leading place among the drugs and in connection with methods for the modern treatment of mycoses. However, it would be incorrect to assume that the problem of the treatment of dermatomycoses has been fully solved. Numerous communications devoted to the description of complications and failures in the employment of recognised antimycotics have been published[6,7]. The spectrum of their activity frequently limited: fungal strains resistant to these antibiotics have appeared. Hitherto, preparations with adequate activities and lacking side effects have been missing from the arsenal of antifungal agents. The acute nature of the problem of the chemotherapy of fungal diseases requires the improvement of the existing medicinal preparations and has stimulated a persistent search for new antimycotics.

The search for active antifungal preparations is based on various classes of compounds[6,11]. Natural antibiotics of the acetylenic series, containing carbofunctional groups in their structure, are extremely promising[8,11-16].

II. NATURAL ACETYLENIC ANTIMYCOTICS

Acetylenic compounds are fairly common in nature as metabolites of many plants and as antibiotics generated by fungi and actinomycetes[8,11-17]. It has been established that acetylenic and polyacetylenic fragments can enter into the composition of the molecules of a wide variety of natural organic substances, but the functions of these highly unsaturated compounds in the metabolism of plants and microorganisms remain not altogether clear[12].

The majority of the acetylenic compounds have been isolated from plant essential oils and fats and from fungal culture liquids[11,13-15]. The classical studies[15-23] provide an idea about the systematic research on natural poly-ynes and the enormous effort by several schools of investigators—those of Sörensen in Norway, Bu'Lock and Jones in England, and Bohlmann in Germany. The experimental data on all natural polyacetylenes known at the beginning of 1971 have been successfully surveyed in a monograph describing many aspects of the problem[12].

Comprehensive studies on the poly-ynes encountered in nature have shown that, apart from their theoretical interest, associated with the elucidation of their role in the biosynthetic processes involving the living cell, they are of considerable practical interest in view of their high biological activity. Many natural polyacetylenes retard the growth of various bacterial and fungal species even at high dilutions. According to Shemyakin's data[8], antifungal activity has been noted among 353 antibiotics (this number has now increased). The pronounced antifungal activity of natural poly-ynes investigated in this respect has attracted particular attention. The best known of these are capillin (I), wyerone (IV), agrocybin (VI), biformene (VII), nemotin (IX), and others.

Capillin has attracted the steady attention of investigators by virtue of its high antifungal activity and comparatively simple structure. Capillin has in fact led to the publication of numerous studies devoted to the synthesis and investigation of the biological properties of analogous and related compounds[24-36]. This diacetylene was isolated in 1957 from the essential oil of *Artemisia capillaris* and the formula of 1-phenylhexa-2,4-diyn-1-one (I) proposed for it was confirmed by synthesis[28,31]:

$$\mathrm{CH_3{-}C{\equiv}C{-}C{\equiv}CH \xrightarrow[C_6H_5CHO]{NaNH_2} CH_3{-}C{\equiv}C{-}C{\equiv}C{-}CHOH{-}C_6H_5 \rightarrow}$$

$$\mathrm{\xrightarrow[AcOH]{CrO_3} \underset{(I)}{C_6H_5{-}CO{-}C{\equiv}C{-}C{\equiv}C{-}CH_3}} \quad .$$

The acetylenic compound (II), called capillene, had been isolated previously[32] from the essential oil of plants of the same genus. It transpired later that it is identical with agropyrene[33] and "dehydroagropyrene"[37].

$$\mathrm{\underset{(II)}{C_6H_5{-}CH_2{-}C{\equiv}C{-}C{\equiv}C{-}CH_3}}$$

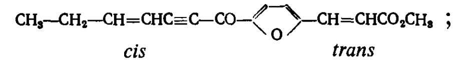
The demonstration of the identity of agropyrene from *Agropyrum repens* and capillene from *Artemisia campestris* and determination of the structure were preceded by research prosecuted by several investigators over a period of almost three decades. Thus Harada[29,30] determined more accurately the formula of capillene and confirmed it by synthesis in accordance with the following scheme:

$$C_6H_5{-}CH_2{-}C{\equiv}CH \xrightarrow[CH_3C{\equiv}CI]{MgBrC_2H_5} \underset{(II)}{C_6H_5{-}CH_2{-}C{\equiv}C{-}C{\equiv}C{-}CH_3} .$$

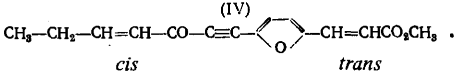
It was shown later that capillene is oxidised to capillin on prolonged storage in air. Both capillene and capillin exhibit an exceptionally strong antimicrobial activity and also high activity against various phytopathogenic fungi. Capillin arrests the growth of dermatophytes in a nutrient medium at very low concentrations (0.25 μg ml^{-1}).[24,28] In tests of its antifungal activity in experiments on animals, capillin proved to be active against *Trychophyton asteroides*[25,38]. Several representatives of aromatic acetylenic compounds closely related to capillin have been isolated from plants of the *Compositae* family: capillon, capillarin, and desmethylcapillin[39-41]. It is noteworthy that an unsaturated hydrocarbon (III) with four conjugated triple bonds, whose antifungal activity surpasses that of capillin, has been detected in extracts from higher plants[42].

$$\underset{(III)}{CH_3{-}CH{=}CH{-}(C{\equiv}C)_4{-}CH{=}CH_2}$$

Natural thienyl- and furyl-poly-ynes with a wide variety of structures exhibit a high antibiotic activity[8,11,12,15,43-57]. Among poly-yne metabolites of higher plants, an extremely effective antimycotic has been detected[43,58,59]—a disubstituted furan derivative. The crystalline compound was isolated from a *Vicia faba* extract. Oxidation of the natural product with potassium permanganate yielded furan-2,5-dicarboxylic acid. According to ^{1}H NMR and mass-spectrometric data, it was possible to postulate two structures, (IV) and (V), for this compound[12,43,58,59]:

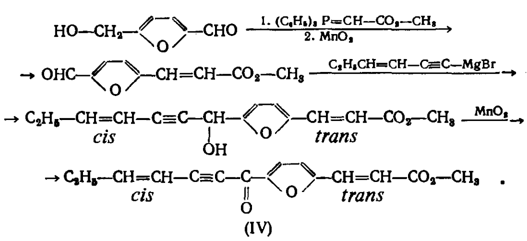


(IV)



(V)

The validity of formula (IV) was demonstrated by synthesis from 5-hydroxymethylfurfural[58,59]:



(IV)

The ketoester (IV), called wyerone, can suppress the growth of many pathogenic fungi—*Alternaria brassicicola*, *Aspergillus niger*, *Uromyces fabae*, and *Glomerella cingaluta*—at a concentration of approximately 10 μg ml^{-1}.

Polyunsaturated products from fungal microorganisms are highly polar substances with functional groups. Powerful acetylenic antimycotics—agrocybin (VI)[60,61] and biformene (VII)[62-64]—have been isolated from the culture liquids of basidiomycetes.

An unstable crystalline triyne (VI) has been isolated by extraction from the culture liquid of the fungus *Agrocybe dura.*[60,61] Analysis of spectroscopic data and specific synthesis showed that agrocybin has the structure of the amide of 8-hydroxyocta-2,4,8-triynoic acid (VI)[65,66]:

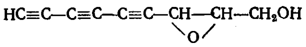
$$HO{-}CH_2{-}C{\equiv}C{-}C{\equiv}CH + HC{\equiv}C{-}COOMe \xrightarrow[CuCl]{O_2}$$
$$\rightarrow HOCH_2C{\equiv}C{-}C{\equiv}C{-}COOMe \xrightarrow{NH_3} \underset{(VI)}{HOCH_2{-}(C{\equiv}C)_3\,CONH_2} .$$

A high antifungal activity is characteristic of agrocybin, but its toxicity is also high: LD_{50} for mice is 60 mg kg^{-1}.[61]

Biformene is an interesting polyacetylenic antibiotic[62-64]. In the study of the antibiotic activity of this poly-yne it was noted that it is active *in vitro* against various representatives of gram-positive and gram-negative microbes and the mycobacteria responsible for tuberculosis. It exhibits a fairly high activity as an antimycotic (0.5–4 μg ml^{-1}), but it did not show a therapeutic effect in tests on animals. After a series of studies, structure (VII) was established for biformene. According to ultraviolet and infrared spectra, its molecule contains a triyne system and an unsubstituted ethynyl group. Since hydrogenation of the natural product led to nonane-1,2-diol, the structure of the triynediol (VII) was proposed for biformene[63,67,68]:

$$\underset{(VII)}{HC{\equiv}C{-}C{\equiv}C{-}C{\equiv}C{-}CH_2{-}CH\,(OH){-}CH_2OH} .$$

The synthetic nona-4,6,8-triyne-1,2-diol (VII), obtained by Bohlmann[69], did not correspond to natural biformene as regards its properties. The epoxide (VIII) proved to be identical with the natural poly-yne[70]:

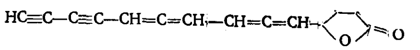


(VIII)

A whole series of similar epoxides were later isolated from plants of the *Compositae* family[71,72].

A fairly large class of compounds, incorporating the allene-diacetylene group as a structural element, has been discovered among natural poly-ynes. Many compounds of this type exhibit a broad-spectrum antimicrobal activity[73-77].

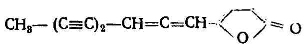
A mixture of antibiotics (IX)–(XII), present in the culture liquids of *Poria tenium*, *Poria corticola*, and the basidiomycete B-841, has been described[73-75]. The pronounced antifungal effect of nemotin (IX) against many strains of various fungi (0.06–16 μg ml^{-1})[74] has been noted. Its activity does not decrease in the presence of blood serum. Nemotin is the lactone of nemotinic acid (X); the biological activity of compound (X) is close to that of (IX) in terms of its bactericidal spectrum, but its fungicidal activity is different.



(IX)

$$\underset{(X)}{HC{\equiv}C{-}C{\equiv}C{-}CH{=}C{=}CHCH\,(OH)\,(CH_2)_2{-}COOH}$$

The reliability of structures (IX) and (X) was confirmed by the study of their infrared spectra and isomerisation products. Comparison of the entire set of chemical and spectroscopic characteristics made it possible to identify in the mixture of metabolites of the B-841 fungus the antibiotics odyssin (XI) and odyssic acid (XII)—the methyl homologues of compounds (IX) and (X) [73-75]:



(XI)

$CH_3—(C≡C)_2—CH=C=CHCH(OH)(CH_2)_2—COOH$.

(XII)

The study of the biologically active products of the metabolism of microorganisms stimulated the development of a new field of organic synthesis—research on new compounds with antifungal properties.

III. SYNTHETIC ACETYLENIC ANTIMYCOTICS

The literature data show that acetylenic compounds have recently aroused interest ss drugs [11,35,43,76-87]. The spectrum of the biological activity of acetylenic compounds is unusually broad: they behave as convulsants, anticonvulsants, local anaesthetics, analgesics, hypotensive agents, ganglion-blocking agents, and antibacterial agents [76], and many acetylenic preparations are frequently more active, less toxic, and more readily assimilated by the organism than their olefinic or saturated analogues. The presence of the triple bond in the molecule apparently lowers the toxicity and improves the degree of absorption and metabolism of certain drugs.

Interest in the analogues of natural acetylenic antibiotics has been shown particularly in the last 10–15 years. During this period, mono-, di-, and vinylacetylenic ketones [11,26,27,35,43,77,83,85,88-93], acetylenic ketoacids [94,95], esters [35,76,77,85,87,96-100], and other acetylenic compounds [11,76-81] were synthesised in order to investigate their biological properties.

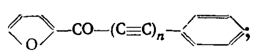
The successful synthesis of complex unsaturated compounds with functional groups has a sound methodological basis in the chemistry of acetylene [11,12,76,100-106]. Many poly-ynes have been obtained by oxidative dimerisation[101,102] and asymmetric condensation[102-104]. They are frequently synthesised in connection with the systematic investigation of acetylenic compounds with properties prediced beforehand[35,36,43,78-80,83-87,90,107-118]. Unfortunately a rigorous scientific theory, which would be able to eliminate empiricism from the synthesis and modification of the molecules of known antibiotics and would enable a purposeful search for new drugs with specific therapeutic activity, is still lacking[119].

The fungicidal activity of natural polyacetylenes depends to a large extent on their structure [12,34,77] and in most cases the activity is rigorously selective, which gives rise to the hope that new synthetic analogues with selective antifungal activity will be obtained [35,43,83-87,110-122].

1. Acetylenic Carbonyl Compounds

The antifungal activity of acetylenic carbonyl compounds is attributed to the presence in their molecules of the conjugated ketoethynyl group [25,26,35,77,123]. The hypothesis of the biological specificity of the ketoethynyl group –CO–C≡C– in the capillin molecule and the assumption that this fragment is responsible for the antifungal effect was formulated in two investigations [25,26]. It was confirmed and justified by extensive experimental data on the synthesis of acetylenes with carbofunctional groups and results amplifying the available information about the influence of various structural elements on fungicidal properties [35,43,83,85-87,90,124-135]. Joint investigations by chemists and microbiologists have shown that any structural changes in the ketoethynyl group (the breakdown of conjugation, the introduction of double bonds) cause an appreciable decrease of activity or a sharp change in the nature of the activity of the preparation [35,43,77,81,83,85-87,90,128,132]. It was found that the nature of the substituents at the CO group and the triple bond has little influence on the antibiotic activity, but determines the irritant action and the pharmocological properties of acetylenes with carbofunctional groups [35,36,81,86,135]. The replacement of the phenyl group in capillin itself by chlorophenyl, methoxy-, and thienyl groups leads to a decrease of the antifungal activity and an increase of the irritant action[27,37]. There are data [86,130,136] showing that the irritant action may be greatly reduced by introducing a hydroxy-group into the α-ethynylketone molecule or by the replacement of the alkyl group by the phenyl group. The increase of the length of the carbon chain of the alkyl substituent to C_4 increases the activity of capillin and capillene analogues, but a further increase in chain length lowers the activity[81].

Many investigators attempted to elucidate the relation between antifungal activity and the degree of unsaturation (the number of triple bonds in the antimycotic molecule)[26,35,83-87,121,133,135]. It was shown [83,86,129] that the second acetylenic fragment introduced into the conjugation chain of furylphenylacetylenic ketones (XIII) enhances the antifugal properties somewhat, but the triynones (XIII, $n = 3$) already show a sharp decrease of both fungistatic and bacteriostatic activities:



; $n = 1, 2, 3$.

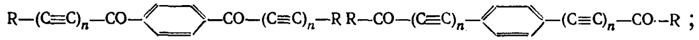
(XIII)

The small biological effect of the triynone (XIII) has been explained [129] by its low solubility in water and its decomposition after the incubation of cultures in a thermostat for many hours. Cases are known where the introduction of a second acetylenic bond into the molecule lowers the antimycotic effect [84,133,134].

Since the use of the known natural antimycotics of the propynone series is precluded by their high toxicity, new methods have been proposed and applied in the search for analogues with low toxicity [35,43,83,137-139] and the known methods have been improved. Fairly extensive data have now been accumulated on the synthesis of α-acetylenic ketones. Surveys of the chemical properties and the methods of synthesis of α-ethynylketones have been published [35,140,141]. The generally accepted methods are not always suitable for the preparation of ketones with other functional groups, owing to the exceptional reactivity of the α-ethynylcarbonyl group. The triple bond in α-ethynylketones is highly activated by the adjacent carbonyl group and readily undergoes various nucleophilic addition reactions. The most rational method for the preparation of ethynylketones is the oxidation of secondary acetylenic alcohols. The use of active manganese dioxide [142] as well as chromium trioxide in sulphuric or acetic acid made it possible to obtain a wide range of acetylenic ketones (XIV)–(XXVI) with various structures by the oxidation of the corresponding alcohols and glycols [35,43,83,85,87,90,99,137,143]:

$R{-}CO{-}(C{\equiv}C)_n{-}R'$;
(XIV) $n = 1, 2, 3$

$R{-}C{\equiv}C{-}CO{-}C{\equiv}C{-}R'$;
(XV)


(XVI) $n = 1, 2$
(XVII) $n = 1, 2$

$R{-}CO{-}(C{\equiv}C)_nCO{-}R$;
(XVIII) $n = 1, 2$

$R{-}CO{-}C{\equiv}C{-}CH{=}CH_2$;
(XIX)

$RR'C(OH)(C{\equiv}C)_n{-}CO{-}R''$;
(XX) $n = 1, 2$

$R{-}C{\equiv}C{-}CO{-}CH{=}CH{-}R'$;
(XXI)

$RR'C(OH)C{\equiv}C{-}CH_2{-}CO{-}R''$;
(XXII)

$RR'C(OH)CH_2{-}C{\equiv}C{-}CO{-}R''$;
(XXIII)

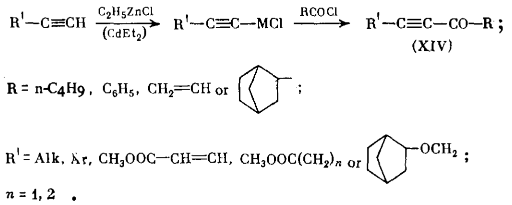
$R{-}O{-}C(R'R'')(C{\equiv}C)_n{-}CO{-}R'''$;
(XXIV) $n = 1, 2$

$R{-}CO{-}C{\equiv}C{-}CH_2Hal$;
(XXV)

$R{-}CO{-}CH_2C{\equiv}C{-}Hal$;
(XXVI)

R, R′, R″ = furyl, pyridyl, thienyl, or norbornyl.

High yields of monoacetylenic and vinylacetylenic ketones, acetylenic diketones, and ketoacid esters have been obtained by the reaction of ethynylzinc or ethynylcadmium reagents, resembling the Iotsich complex in terms of their reactivity, with the chlorides and anhydrides of aliphatic and aromatic acids [85,113-116]:



$$R'{-}C{\equiv}CH \xrightarrow[(CdEt_2)]{C_2H_5ZnCl} R'{-}C{\equiv}C{-}MCl \xrightarrow{RCOCl} \underset{(XIV)}{R'{-}C{\equiv}C{-}CO{-}R};$$

R = n-C_4H_9, C_6H_5, $CH_2{=}CH$ or ;

R′ = Alk, Ar, $CH_3OOC{-}CH{=}CH$, $CH_3OOC(CH_2)_n$ or ;

$n = 1, 2$.

Ethynylketones (XIV) are active against *Trichophyton gypseum* and a ketone with the norbornene substituent at the carbonyl group showed a distinct therapeutic effect on an experimental model of dermatomycosis [85,86].

The pentadiynone group, analogous to capillin, is retained in the diacetylenic ketones (XIV, $n = 2$), obtained by the oxidation of secondary diacetylenic alcohols with manganese dioxide [35,83,85,126,127]:

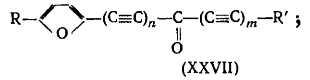
$$\left.\begin{array}{l} R{-}CHOH{-}C{\equiv}CH + BrC{\equiv}C{-}R' \xrightarrow{H_2Net} \\ R{-}CHO + HC{\equiv}C{-}C{\equiv}C{-}R' \xrightarrow{MgBrEt} \end{array}\right| \rightarrow R{-}CHOH{-}(C{\equiv}C)_2{-}R' \rightarrow$$

$$\xrightarrow{MnO_2} \underset{(XIV)}{R{-}CO{-}(C{\equiv}C)_2{-}R'} .$$

Triacetylenic and tetra-acetylenic ketones have been obtained in accordance with the same scheme [35].

In order to improve the stability of polyunsaturated capillin-like compounds, use was made of silylacetylenic derivates with a high fungicidal activity in relation to *Trichophyton gypseum* and *rubrum*. [117]

In contrast to benzoylacetylenes, furoylacetylenes (XXVII) exhibit a strong antifungal activity combined with a lower toxicity. This observation initiated systematic research into furylalkynes [35,43,83,86]. The monoacetylenic ketone 1-(2-furyl)-5-phenylpent-4-yn-3-one is known [92] to be active not only against *Trichophyton* but also against *Candida* and many other fungi.

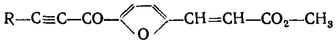


(XXVII)

$n = 0, 1$; $m = 0, 1$; R=H, Br, Cl, I, NO_2, or COOH;

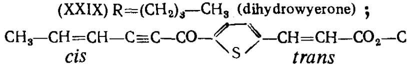
R′ = alkyl, aryl, 5-bromo-2-furyl, OH, OCH_3, or OC_2H_5.

A fairly high activity against pathogenic fungi, resembling that of the natural precursor wyerone (IV), is shown by its synthetic analogues (XXVIII)–(XXX) [44,58,59]:



(XXVIII)–(XXIX)

(XXVIII) R=*cis*-$CH{=}CH{-}CH_3$ (norwyerone) ;
(XXIX) R=$(CH_2)_3{-}CH_3$ (dihydrowyerone) ;



(XXX)

The high antifungal activity of the ketones (XIV) has been noted in a number of patents [89,92,144-148]: data obtained in recent years [35,36,83,85,86,118,144-156] are evidence showing that studies on the practical applications of these substances have been carried out, for example, in the fight against the fungal diseases of plants [150]. A pronounced antifungal activity is characteristic of all the ketones tested. Dermatophytes are particularly sensitive to acetylenic ketones. A common property of ethynylketones is their weak activity against strains of yeast-like fungi and actinomycetes [35,43,83,85,86]. Mention should be made of data [81,82,85,86,122,135] concerning the activity of ethynylketones against the tuberculosis mycobacterium. The high tuberculostatic activity of α-ethynylketones is shown not only *in vitro* but also *in vivo* [35,85,86,135].

Presumably the likely mechanism of the antibiotic activity [157-160] of α-acetylenic ketones is analogous or similar to the mechanism proposed for the activity of $\alpha\beta$-diunsaturated ketones. The antibiotic effect of $\alpha\beta$-diunsaturated ketones has been explained in well known studies [161,162] by their tendency to interact with the sulphhydryl groups of enzymes, which are important for the vital activity of microorganisms. Reactions of this kind with nucleophiles of the SH type are in fact characteristic of ethynylketones to an even greater extent than of vinylketones. The mechanisms of the action of various antifungal substances are not the same. There are data showing [160] that acetylenic derivatives exhibit a more restricted activity on the cytoplasmic membrane than polyenes. It may be that the selective antifungal activity of the acetylenic preparation is associated with the breakdown of the functions of the cell wall, although it need not be of the same type as in polyenes [160]. The tendency to explain the mechanism of the action of antibiotics at a molecular level has been dominant in recent years [9,158,163,164]. The quantum-mechanical treatment of pharmacological problems—the correlation of activity with parameters of the electronic structures of active compounds—appears to be extremely promising [165]. In future we may expect a sharp increase of attention devoted to this problem, without the solution of which the specific synthesis of therapeutically valuable derivatives of natural antibiotics appears to be impossible.

2. Acetylenecarboxylic Acids and Their Derivatives With Antifungal Activity

Amongst natural poly-yne acids and their derivatives, a number of powerful antimycotics have been discovered [8,12,65,73-75], which led to a vigorous search for new antifungal agents based on unsaturated carboxylic acids. Even the structurally simplest propiolic acid and its esters are active against many fungi, while methylpropiolic acid also possesses antibacterial properties. A further increase in the number of methylene groups reduces the bacteriostatic activity and enhances the fungistatic activity. Judging from patent data [166-168], ω-iodoalkynoic acids (XXXI) and their esters (XXXII) are also active against mycoses [169,170]:

$$\underset{(XXXI)}{IC{\equiv}C{-}(CH_2)_n{-}COOH};\ n = 1{-}7\quad \underset{(XXXII)}{IC{\equiv}C{-}(CH_2)_8{-}COOR} .$$

In experiments on the mycelia of *Trichophyton* and a yeast-like fungus a study was made of acetylenic acids derived from furan[171-173]. It was shown that the presence of the ketoethynyl group combined with the furan ring in the molecule promotes fungistatic activity, but the introduction of substituents (a bromo- or nitro-group) in the 5-position in the furan ring reduces the fungistatic activity and sharply enhances the bacteriostatic activity.

The esters (XXXIII) of acetylenecarboxylic acids and polyhydric alcohols suppress the growth of bacteria and fungi even at a very low concentration[174]:

$$HO{-}(CH_2)_n{-}OH + R{-}C{\equiv}C{-}CO_2H \xrightarrow[H^+]{C_6H_6} R{-}C{\equiv}C{-}COO(CH_2)_nOCO{-}C{\equiv}C{-}R\ .$$

(XXXIII)

The fungistatic activity of dicarboxylic acid esters is somewhat greater than that of the acids themselves, the second carboxy-group having little effect on the activity[77,175,176]. It has been suggested that different esters of acetylene-dicarboxylic acid as well as its salts be used to control the fungal diseases of rice[177].

In the series of dimethyl dicarboxylate esters of the type $(CH_3OC_2{-}(CH_2)_2{-}(C{\equiv}C)_n{-}(CH_2)_2{-}CO_2CH_3$ (XXXIV) the fungicidal activity increases sharply on passing from diacetylenic to tetra-acetylenic derivatives[121]. A similar behaviour has also been observed for monocarboxylic acids of type (XXXV)[121]:

$$C_4H_9{-}(C{\equiv}C)_n{-}R\ ;$$

(XXXV)

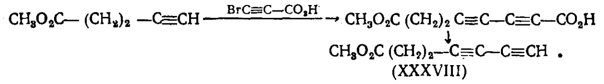
$R{=}(CH_2)_m{-}CO_2H$, CO_2H, or $CH{=}CHCO_2H$; $m = 0{-}2$.

Kucherov and coworkers[121,178] investigated systematically the pathways leading to the formation of many polyunsaturated mono- and di-carboxylic acids. In order to elucidate the dependence of biological activity on structure, the nature of the functional groups, and the number of triple bonds, acids of two types, (XXXVI) and (XXXVII), were examined[178]:

$$R{-}(C{\equiv}C)_m{-}(CH_2)_n{-}COOH \qquad R{-}(C{\equiv}C)_m{-}(CH{=}CH)_n{-}CH_2CH_2{-}COOH\ .$$

(XXXVI) (XXXVII)

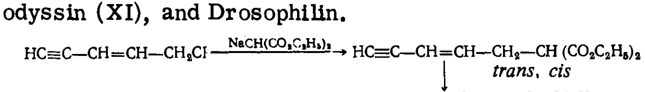
The Chodkiewicz condensation[102-104] served as a basis for the syntheses, which required the development of easy methods for the formation of fragments with a terminal acetylenic bond, as in compound (XXXVIII):



$$\begin{array}{l} CH_3O_2C{-}(CH_2)_2{-}C{\equiv}CH \xrightarrow{BrC\equiv C-CO_2H} CH_3O_2C(CH_2)_2C{\equiv}C{-}C{\equiv}C{-}CO_2H \\ \qquad\qquad\qquad\qquad\qquad\qquad \downarrow \\ \qquad\qquad\qquad\qquad\qquad CH_3O_2C(CH_2)_2{-}C{\equiv}C{-}C{\equiv}CH\ . \end{array}$$

(XXXVIII)

A series of polyunsaturated acids (XXXVII) have been obtained (in yields up to 50%) by the oxidative condensation of the vinylacetylenic acid (XXXIX) and its bromide with different acetylenic acids, alcohols, and hydrocarbons[178]. Carboxylic acids (XXXVII) containing the vinylacetylene group are related to the natural antimycotics—nemotin (IX), odyssin (XI), and Drosophilin.

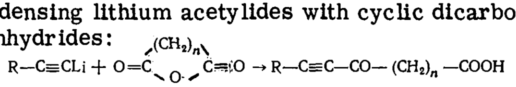


$$\begin{array}{l} HC{\equiv}C{-}CH{=}CH{-}CH_2Cl \xrightarrow{NaCH(CO_2C_2H_5)_2} HC{\equiv}C{-}CH{=}CH{-}CH_2{-}CH(CO_2C_2H_5)_2 \\ \qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad \downarrow \quad \textit{trans, cis} \\ \qquad\qquad\qquad\qquad\qquad HC{\equiv}C{-}CH{=}CH{-}CH_2CH_2CO_2H\ . \\ \qquad\qquad\qquad\qquad\qquad\qquad\qquad \textit{trans} \end{array}$$

(XXXIX)

Many vinylacetylenic acids exhibit a powerful selective activity in relation to certain types of pathogenic fungi at concentrations (*in vitro*) comparable to those of the strongest antimycotics (capillene, odyssin).

The method for the preparation of unsaturated keto-acids developed by Bergel'son et al.[95] was extended by Bergel'son and Grigoryan to the synthesis of ketoacids with terminal double and triple bonds[179]. Ketoacids of the type $R{-}C{\equiv}C{-}CO{-}(CH_2)_n{-}COOH$ (XL) have been obtained by condensing lithium acetylides with cyclic dicarboxylic acid anhydrides:



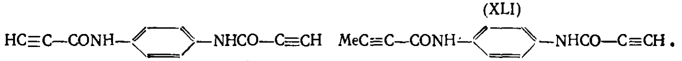
(XL)

Acetylenic ketoesters with low toxicity, which suppress *in vitro* the pathogenic dermatophytes *Microsporon lanosum* and *Achorion schönleini* at concentrations of 1–2 $\mu g\ ml^{-1}$ and *Trichophyton gypseum* at a concentration of 6 $\mu g\ ml^{-1}$, have been obtained by this method. It is noteworthy that the high antifungal activity of the unsaturated ketoester (XL, $R{=}C_4H_9$, $n = 3$) depends on the presence of its molecule of the conjugated ethynylketone group, since its ethylene analogue is less active and the corresponding saturated ketoester altogether fails to suppress the growth of the above fungi[95].

Fungicidal agents have been found recently not only among the esters[160,169,170,174,180-184], but also among the amides of acetylenic acids[185-189]. The propiolamides (XLI)-(XLIII) are particularly active[135,186]:

$$HC{\equiv}C{-}COCl + H_2N{-}(CH_2)_6{-}H_2N \rightarrow HC{\equiv}C{-}CONH{-}(CH_2)_6{-}HNCO{-}C{\equiv}CH\ ;$$

(XLI)



(XLII) m.p. 228° (XLIII) m.p. > 300°

In order to obtain compounds inhibiting the growth of microbes, studies have been made[190-193] of the synthesis and microbiological properties of acetylenic aminoacids. L-3-(2-propynylthio)alanine (XLIV) may be used as a fungicide active against certain parasitic fungi[191]:

$$HC{\equiv}CCH_2Br + HSCH_2CH(NH_2)COONa \xrightarrow{NH_3} HC{\equiv}C{-}CH_2S{-}CH_2{-}CH(NH_2){-}COOH\ .$$

(XLIV)

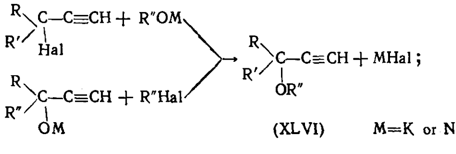
3. Propargyl Ethers

A series of studies have been made and a number of patents have been taken out concerning the synthesis and biological properties of aryl propargyl ethers (XLV), many of which are powerful fungicides[85,87,97-99,131,143,194-210]:

$$Ar{-}Y{-}CH_2{-}C{\equiv}C{-}R \quad Y{=}O \text{ or } S;\quad R{=}Hal \text{ or } H.$$

(XLV)

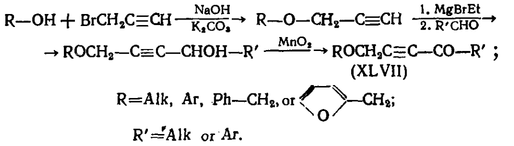
Direct and indirect methods are known for the preparation of ethers from acetylenic alcohols. Terminal propargyl ethers (XLVI) are usually obtained by the interaction of propargyl halides with alkoxides, derived from saturated alcohols, and phenoxides or by the interaction of alkoxides derived from acetylenic carbinols with alkyl halides. The ethers (XLVI) can serve as key substances in the synthesis of a wide variety of bifunctional acetylenes and aminopropargyl ethers exhibiting antifungal activity:



(XLVI) M=K or Na.

A convenient method[203,204] involves the hydroxypropargylation of norbornenes at the strained double bond in the presence of boron trifluoride etherate, which leads to *exo*-propargyloxynorbornanes in satisfactory yields (40 to 97%).

A specific synthesis of new antimycotics made it possible to develop an optimum version of the synthesis of propargyloxyketones (XLVII)[35,87,99]:



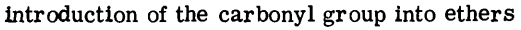
$$R{-}OH + BrCH_2C{\equiv}CH \xrightarrow[K_2CO_3]{NaOH} R{-}O{-}CH_2{-}C{\equiv}CH \xrightarrow[2.\ R'CHO]{1.\ MgBrEt} ROCH_2{-}C{\equiv}C{-}CHOH{-}R' \xrightarrow{MnO_2} \underset{(XLVII)}{ROCH_2C{\equiv}C{-}CO{-}R'}\ ;$$

R=Alk, Ar, Ph—CH₂, or

R′=Alk or Ar.

The introduction of the carbonyl group into ethers derived from acetylenic alcohols made it possible to increase their antifungal activity[82,87,99,130,131]. The study of the antibiotic properties of ketoethers in relation to a large series of strains *in vitro* showed that they exhibit a high antifungal activity, suppressing the growth of dermatophytes at concentrations of 1.2–1.56 μg ml^{-1}. The nature of the substituents at the ether and carbonyl groups plays a certain role, but it was not possible to establish a correlation between the structure of the compounds and their activity[87,99].

Fungistatic and germicidal agents have been discovered among benzthiazolyl propynyl sulphides[211,212]:



(XLVIII)

X = 5-Cl, 4-Me, 6-EtO, etc.

Unsubstituted alkyl ethynylvinyl sulphides HC≡C–CH=CHSAlk (XLIX) proved to be active against certain species of mould developing in PVC coatings in tropical climates[111].

4. Acetylenic Alcohols

The antimycotic activity of monoacetylenic alcohols is low compared with the corresponding carbonyl compounds[77,81,85,86,123], but the inhibiting activity of vinylacetylenic and diacetylenic alcohols is higher. Interesting reports have been published[213-216] about acetylenic carbinols as fungicides. Compounds having the general formula R–C≡CCXCH=CH–R′ (L), where R = phenyl or naphthyl and X = H or OH, are active against moulds on plants[213].

Fungistatic activity is also shown by alcohols with a short chain having a phenyl substituent adjacent to a triple bond[77,123]. The introduction of a double bond into short-chain primary alcohols in a position which results in conjugation with the triple bond enhances the fungistatic activity, particularly if the phenyl substituent and the triple bond are at the end of the molecule. The vinylacetylenic carbinol (LI) exhibits fungistatic activity; the same properties are also shown distinctly by the secondary alcohol (LII), in which the double bond is not conjugated with the triple bond, occupying the $\alpha\beta$-position relative to the carbinol carbon:

$$\underset{(LI)}{C_6H_5{-}C{\equiv}C{-}HC{=}CH{-}CH_2OH}\ ;$$

$$\underset{(LII)}{C_6H_5{-}C{\equiv}C{-}CH\,(OH){-}CH{=}CH{-}C_6H_5}\ .$$

Symmetrical acetylenic and diacetylenic glycols show a very insignificant fungistatic activity, while the asymmetric compounds are more active fungicides. The biological activity apparently depends on the effect of the functional groups on the polarisation of the triple bond[11,77,123]. By varying the structural fragments in the molecule (in order to find highly active water-soluble antimycotics), it was shown that the hydroxy-group in acetylenic ketones removes the irritant effect, increases somewhat the solubility of the compounds in aqueous media, and hardly alters the antifungal activity[35,80,86,131,136]. The antifungal activity of acetylenic ketoacid esters (XL)

$$n\text{-}C_4H_9C{\equiv}C{-}CO\,(CH_2)_3\,COOMe$$

disappears when hydroxy-groups are introduced into their molecules[95].

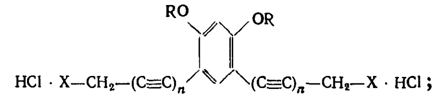
5. Nitrogen-containing Acetylenes

The presence of the amino-group as a rule increases the biological activity of acetylenic compounds[11,76,107,123,217,218]. The spectrum of the pharmacological activity of acetylenic amines is broad, but there have been no comprehensive and specific studies of the biological properties of acetylenic amines.

Data have been published recently on the antifungal activity of aminomethyl derivatives of aryl- and heteryl-acetylenes (LIII) with regularly varying structures[219-220]:

$$Ar\,(C{\equiv}C)_n\,H + HCHO + HNRR' \xrightarrow{CuCl} \underset{(LIII)}{Ar\,(C{\equiv}C)_n\,CH_2NRR'}\ .$$

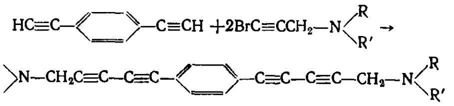
Kotlyarevskii and coworkers[219-223] investigated systematically the spectrum of the biological activity of amino-derivatives of arylpoly-ynes (LIV):



(LIV)

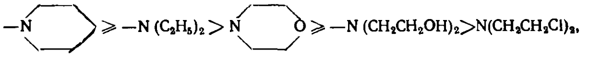
X = amine.

Conditions were found for the aminomethylation of diacetylenic compounds in which the main products are either monoamines or diamines. A monoamine may be used to obtain mixed diacetylenic diamines for oxidative dimerisation to tetra-acetylenic diamines or for the formation of triacetylenic diamines (LV)[223]:



(LV)

The majority of the compounds tested exhibit a pronounced bacteriostatic activity in relation to acid-resistant bacteria. The structures of the aromatic, acetylenic, and amine fragments influence appreciably the efficiency of their action. The introduction of an electron-donating substituent (CH_3O, CH_3) into the benzene ring and the increase of the degree of unsaturation of compounds (LIII, $n = 2$) result in an increase of biological activity. A further increase of the number of acetylenic groups ($n > 2$) results in a sharp decrease of activity. As the structure of the amine component of the molecule is varied, the antibacterial activity diminishes in the sequence

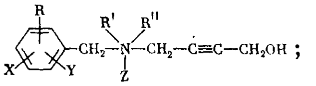


apparently in parallel with the decrease of the basicity of the amines[219]. It is of interest[84,134] that, among aryl-substituted aminoacetylenic compounds (LIV), amines with a single triple bond in each aliphatic chain are active against fungi. The introduction of the second triple bond into any aliphatic chain leads to the disappearance of activity.

The amino-group can form salts and, like the carboxy-group, may increase the solubility of the preparations in water[35,83-87,118]. In many cases this ionogenic fragment is introduced into the molecule by the Mannich reaction in accordance with the general mechanism

$$RC{\equiv}CH + CH_2O + HNR_2 \rightarrow RC{\equiv}C{-}CH_2NR_2 \quad .$$

In order to synthesise water-soluble antifungal preparations, certain derivatives of furan with functional groups[83], propargyl ethers derived from phenol and β-naphthol[118], a series of terminal acetylenic derivatives of bicycloheptane[85,203,204], and aryl- and heteryl-acetylenes[84,222] were aminomethylated. A series of quaternary ammonium compounds (LVI) exhibiting antifungal activity have been obtained by the quaternisation of tertiary amines[217]:



(LVI)

R', R'' = Alk; R = Alk (8-16 C atoms);

X, Y = CH_3, C_2H_5;

Z = salt-forming anion .

By employing a fungicidal solution (0.001%) of the hydrochloride of [1,4-bis-(2,4,6-trichlorophenoxy)-2-butynyl]dimethylamine and decahydroquinoline in the treatment of the *Verticillium* wilt of the cotton plant, an appreciable improvement of the crop was achieved[118].

Certain acetylenes whose structure incorporates a nitrogen-containing heterocycle are powerful antimycotics[208,209,224]. Thus 5-(3-iodopropargyloxy)-2-methylthiopyrimidine[209] is active (0.1–20 mg $litre^{-1}$) even against yeast-like fungi. It is noteworthy that the structures of these antimycotics frequently include the hydroxypropargyl fragment[208,209].

6. Acetylenic Hydrocarbons

Only a few poly-ynes with conjugated triple bonds have been investigated hitherto as antimicrobial preparations[77,123,225]. Apparently there is a relation between the number of conjugated triple bonds and antibiotic activity, but its nature is insufficiently clear[77].

Aliphatic hydrocarbons in which the triple bonds occupy the 1-ω-position exhibit a very weak antimicrobial activity[123]. In certain cases[226,227] halogeno-derivatives of hydrocarbons are highly active fungistatic agents. Halogenoalkynes are used to protect fruit from rotting. It may be that the biological effect of the most active iodoalkynes is to some extent due to the action of iodine[77,227].

In conclusion one should note that quantitative data on the antibiotic activities quoted by various authors do not always agree. This can probably be accounted for in the first place by the lack of standard strains (owing to the wide occurrence of cultures of microorganisms adapted to antibiotics) and in the second place by the lack of a sensitive method for the determination of the minimum inhibiting concentrations. Despite its approximate and fragmentary nature, the available information about biological activity make possible not only a qualitative but also a quantitative assessment of many compounds and assists in discovering specific relations. Although screening has not as yet become obligatory for all acetylenes with functional groups, interest in these compounds and the development of methods of synthesising them are to a large extent related to the prospect of investigating their biological properties[35,36,43,76-80,83,85,87]. However, biological tests are frequently episodic in character or are replaced by *a priori* guesswork.

Despite the considerable interest in the class of acetylenic antimycotics, the problem of their activity is largely considered at the level of *in vitro* tests. The decisive factor in the solution of the problem of the possible employment of this class of antimycotics as therapeutic agents is *in vivo* tests. Such studies are a problem for the future, although individual reports on this topic have already been published[25,35,85-87,99,135]. Since material costs are not the dominant factor in the study of drugs, the employment of acetylenes in this field is likely to be still greater in the future.

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The Effect of Ionising Radiation on Dissolution Processes

V.V.Gromov

The influence of various effects associated with the preliminary exposure to ionising radiation (γ-quanta, accelerated electrons, heavy particles) of a solid during its dissolution in aqueous media is analysed, particular attention being devoted to the relation between the rate of dissolution and the radiation-induced charge on irradiated and radioactive substances.
The mechanism of the intensification of the dissolution process when the entire solvent-solid system is irradiated is analysed in relation to the dissolution of uranium oxides in sulphate and carbonate solutions. Procedures involving the employment of ionising radiation for the regulation of the rate of dissolution of solids are considered.
The bibliography includes 105 references.

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I. INTRODUCTION

In many technological schemes dissolution is one of the principal operations which limits the economic parameters of the entire process. For this reason, the search for methods of improving the technology of the dissolution process is being prosecuted continuously. In this sense ionising radiation may be a very effective means of intensifying the dissolution of solids under certain conditions. However, despite the undoubted importance of the study of the influence of ionising radiation on the transfer of various substances to the liquid phase, until recently no systematic research in this field has been made.

The first report, by Simnad and Smoluchovski[1], concerning the considerable increase of the rate of dissolution of iron(III) oxide in hydrochloric acid after irradiation of the oxide with protons having an energy of 260 MeV was published in 1955. After this, the efforts of investigators were for a long time concentrated on the study of the radiation-stimulated corrosion and dissolution of various metals and alloys, which was dictated, and is still dictated, by the requirements of "atomic technology".[2]

Various crystalline inorganic salts remain virtually uninvestigated. These include alkali metal halides and numerous oxyacid salts, many of which are widely used in the processing of nuclear materials[3]. The present review is in fact devoted to the dissolution of inorganic salt crystals which have been irradiated with γ-quanta, electrons, and heavy particles. Analogous examples involving metals and organic substances are quoted only as an illustration in the description of the main results[3]. One should note that no reviews have been published hitherto on the effect of ionising radiation on the kinetics of the dissolution of crystalline inorganic compounds. In the present survey an attempt is therefore made to discuss certain aspects of this complex phenomenon, to give a systematic account, to analyse critically the results obtained, and to outline the likely future use of ionising radiation for the regulation of dissolution processes.

The intrinsic mechanism of the dissolution of various simple and complex substances is not considered. It is assumed that the reader is familiar with this problem, which is dealt with in specialist publications[4-6].

II. THE INFLUENCE OF DISSOLUTION CONDITIONS ON THE EFFICIENCY OF THE ACTION OF IONISING RADIATION

The first report about the influence of γ- and X-radiation and of a stream of neutrons on the dissolution of ionic crystals was published as late as 1961.[7] The authors were able to show that the rate of dissolution of sodium chloride after irradiation is a structure-sensitive factor and depends on the nature and concentration of radiation-induced defects. Subsequently this type of research was extended to the accumulation of quantitative data concerning the influence of radiation on the dissolution of crystalline substances in water and aqueous solutions. It was found that the radiation effect depends to a large extent on the dissolution conditions.

Two regions in the dissolution process are usually distinguished: the diffusion region, regulated by processes involving the transport of material in the liquid phase, and the kinetic region, in which the rate of dissolution depends in many aspects on the properties of the solid[4,5]. It is known that, for the majority of ionic compounds, the stage involving the interaction of the solvent with the ions located on the surface of the solid takes place almost instantaneously and the rate of dissolution is determined by diffusion processes in solution. In this case the influence of radiation-induced defects may be obscured, since mass transfer in the liquid phase is the slowest stage in the dissolution process. However, for a whole series of compounds (with low and sparing solubilities) the transition of salt ions into the solution is fairly slow and the process as a whole depends on the rate of interaction of the solvent with the solid, i.e. on its nature and structure, and evidently on the presence of radiation-induced defects (if these exist).

The distinctive features of the heterogeneous dissolution process controlled by diffusion are as follows:

(1) dependence of the rate of the process on the rate and direction of motion of the solvent;

(2) dependence of the rate of dissolution on the diffusion coefficient and the viscosity of the liquid in the boundary layer at the surface of the solid in which the dissolved substances or reaction products accumulate;

(3) comparatively low temperature coefficients of the rate of dissolution.

Non-diffusional dissolution (kinetic region) has the following characteristic features:

(1) as a rule relatively low absolute dissolution rate constants (K_v);

(2) invariance of the dissolution rate constant K_v for different rates of stirring;

(3) rapid increase of the coefficients for the rate of dissolution v with temperature.

The above features permit the conclusion that in the kinetic region the transfer of the molecules (ions) of the solid to the liquid phase is determined by the chemical interaction of the compound undergoing dissolution with the solvent. Under these conditions, the dissolution rate constant is in fact a structure-sensitive quantity, whose value is determined by the properties of the solid, such as the type of bond between the crystal lattice elements, the number and nature of the defects, the lattice energy, the type of crystal structure, etc. Naturally dissolution under these conditions is of greatest interest for the study of the influence of radiation-reduced defects on the transfer of ions or molecules or solids to the liquid phase.

The initial postulate of the modern theory of dissolution is the recognition of the existence of a boundary layer of solution at the surface of the solid with composition different from that corresponding to the state of saturation. Accordingly, the equation for the rate of dissolution of the majority of compounds in water can be expressed as follows[4]:

$$\mathrm{d}c/\mathrm{d}t=\frac{\gamma D}{D+\delta\gamma}\,S\,(c_0-c_t)^n\,, \tag{1}$$

where D is the diffusion coefficient, γ the rate coefficient of the interfacial process, δ the effective thickness of the boundary layer, S the surface area of the compound undergoing distribution, n the order of the dissolution reaction, c_0 the solubility of the given compound, and c_t the concentration of the given compound in solution at time t. It is readily seen from Eqn. (1) that the dissolution rate constant corresponding to a constant volume of the liquid phase is defined by the expression

$$K_v=\frac{\gamma D}{D+\delta\gamma}\,. \tag{2}$$

The order of the dissolution reaction in water is normally unity for the vast majority of compounds. Depending on the relation between the empirical coefficient γ and D/δ, a real dissolution process can have a diffusional or kinetic (interfacial) mechanism. In the latter case the entire process is determined by the kinetics (mechanism) of the interaction of the solvent with the surface of the solid. In conformity with these ideas, three main types of dissolution are possible:

(1) Purely diffusional: $\gamma \gg D/\delta$, i.e. $K_v \to D/\delta$ (diffusional region of the dissolution process);

(2) purely kinetic: $\gamma \ll D/\delta$, i.e. $K_v \to \gamma$ (kinetic region of the dissolution process);

(3) diffusion-kinetic region of the dissolution process, characterised by comparable rate coefficients for the interfacial and diffusion processes: $\gamma \simeq D/\delta$.

Usually the transition to the kinetic dissolution conditions is attained by increasing the rate of stirring of the liquid phase. The concentration difference between the surface layer and the bulk of the solution then becomes insignificant and diffusion processes may be neglected. One should also note that under industrial conditions it is more convenient to carry out the process in the kinetic region, since the removal of the substance undergoing dissolution into the bulk of the solution as a result of the motion of the liquid is then faster than in the diffusional region.

In the study of dissolution processes, experimental problems are of primary importance. Particular attention must be devoted to the reproducibility of the hydrodynamic experimental conditions. Failure to meet this requirement leads to considerable discrepancies between the results even in a series of seemingly identical experiments. Virtually any defects in crystal structures influence the rate of transfer of the ions from the solid to the liquid phase under kinetic dissolution conditions, where the rate limiting stage is the interaction of the species of the solvent and the solid. For example, it has been shown[7] that, when NaCl crystals irradiated with X-rays are dissolved, the effect of radiation is not manifested in any way under diffusional conditions, being appreciable only under kinetic conditions. In experiments with irradiated crystals it is therefore necessary to make sure in the first place that the process proceeds via a diffusional mechanism.

In the study of the role of radiation-induced defects in the dissolution of salts experiments are usually performed with a limited amount of solvent, i.e. under conditions where Eqn. (1) is valid. The rate of dissolution, i.e. the variation of the quantity dc/dt with time, dose, intensity of irradiation, and other parameters is selected as the structure-sensitive characteristic. The majority of conclusions concerning the influence of irradiation on dissolution have been reached precisely by studying the dependence of v on the magnitude of the effects of radiation. However, the rate of dissolution is not a fully reliable criterion of the given process, because it depends [see Eqn. (1)] on the surface area of the crystals and very frequently also on their shape and the micro-relief of the crystal faces.

Even in the kinetic region, v depends strongly on the concentration of the substance undergoing dissolution in the liquid phase (apart from the dependence on S). Furthermore, in the initial stage of the process the rate of dissolution is frequently affected by different random factors, which are difficult to control. With increase of the concentration of the dissolved substance in the liquid phase, the accuracy of the determination of c_t diminishes. As a result of all these factors, the conclusions reached on the basis of the variation of v ultimately become to a large extent qualitative.

A more objective parameter, which characterises the dissolution of the solid, is evidently the dissolution rate constant, which is independent of the variation of the surface area of the crystals during dissolution†.

If it is desirable to obtain a more rigorous relation between the nature and concentration of the radiation-induced defects and the dissolution of the irradiated specimen uncomplicated by the influence of "structure-surface" factors, it is necessary to determine the values of K_V.[8]

It should be noted that, when v_{irr} and $v_{non\text{-}irr}$ are compared, a case may be encountered where the rates of dissolution of the same specimen differ in magnitude but change to the same extent under the influence of irradiation. Naturally the ratio $v_{irr}/v_{non\text{-}irr}$ will then differ from unity and on this basis it would seem possible to conclude that the point defects generated by irradiation affect the entire process[7,9,10]. However, under these conditions K_V does not change, since it is determined from the slope of the curves relating v/S_t to $c_0 - c_t$.

When $v_{irr}/v_{non\text{-}irr}$ changes, all the observed effects may be associated with the breakdown of the surface structure, a change in the surface area, micro-cracking or sintering, etc. If K_V is determined, all the surface effects are usually excluded and the relation between (the number of) radiation-induced point defects and the rate of dissolution of the irradiated crystal is revealed in a pure form, since the dissolution rate constant characterises the number of species of the solid abstracted under the influence of the solvent per unit surface and per unit time.

Furthermore, attention must also be drawn to the influence of the concentration of the dissolved salt in the liquid phase c_t, which affects dc/dt according to Eqn. (1).

The choice of the method and the conditions for the dissolution of the given compound after its irradiation are determined by the fact that point (and linear) defects generated by the radiation are manifested most effectively at low rates of dissolution[14-18]. This is because, for high rates of the given process, the entire surface of the solid in contact with the solvent is "operative" (the influence of the defects is blurred) and, for low values of v, the dissolution takes place at the weakest site—at the defects whose linkages with the crystal matrix are deformed[12-18].

If in the study of dissolution kinetics it is necessary to detect fine effects associated with structural changes in the crystal, one must carry out experiments with low rates of dissolution. For readily soluble salts, this can be achieved using virtually saturated initial solutions[11-13]. Under these conditions, dc/dt varies very strongly even when the crystal structure is altered only slightly. For sparingly soluble compounds, there is no such limitation on the concentration of the solvent.

For example, experiments have been carried out[11-13] with NaCl, KCl, KBr, LiF, and KI in almost saturated solutions, where dc/dt was low and the dissolution did not occur from all the surface points behaving as single "active centres", but only at sites where defects accumulated. Using this method, it was possible to detect many side effects in the dissolution of irradiated crystals.

III. DISSOLUTION OF COMPOUNDS IRRADIATED WITH HEAVY PARTICLES

All the known defects in crystal structures (point, linear, two-dimensional, or three-dimensional defects) may be formed as a result of the irradiation of solids by a particular type of ionising particle.

The displacement of atoms in the crystal lattices of solids is one of the main effects of bombardment by heavy particles (neutrons, protons)[19]. Naturally this is accompanied by ionisation and excitation processes with formation of various "electronic" defects with all subsequent transformations of the kind occurring on γ-irradiation.

The relation between electronic defects and their complexes and dissolution processes has been shown experimentally to be very complex and it is extremely difficult to predict beforehand the nature of their influence on the rate of dissolution. The role of the displacement of atoms, which facilitates the transfer of the ions of the solid to the liquid phase as a result of the weakening of the bond between the displaced atom and the crystal lattice, is clearer. One should also bear in mind that the influence of the same type of defects on the properties of solids of different kinds may differ sharply. The main effects in

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† However, K_V may depend also on the surface relief. It is therefore more correct to compare the values of K_V for specimens with identical surface topographies.

metals are linked with the displaced atoms. On the other hand, for ionic crystals, electronic defects are of decisive importance.

The macrodefects in the structure of the surface of the irradiated crystals have a considerable influence on the dissolution, such defects including evaporation pits, growth projections, radiation-induced cracking, and partial fusion of rugosities, which is observed both on irradiation with electrons[20-23] and on bombardment with heavy particles[24-27]. One should note that irradiation does not always create an excess concentration of defects. It sometimes happens that, following radiation annealing, the crystal actually becomes more perfect owing to the decrease of the number of "biographical" defects[19]. Furthermore, the concentration and nature of radiation-induced defects arising on storage of irradiated crystals usually change gradually as they interact with one another. There is a simultaneous alteration also in the properties of the given specimen. Consequently, dissolution may in some cases be accelerated after a given specimen is acted upon by radiation, while in others the dissolution of the same specimen may be retarded. This has in fact been observed experimentally.

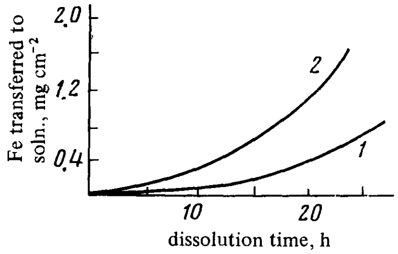

Figure 1. The rate of dissolution of Fe_2O_3 in 1 N HCl after irradiating the oxide with protons[1]: 1) non-irradiated specimen; 2) irradiated oxide; temperature 30°C.

Bombardment with neutrons or any accelerated heavy particles, which causes profound and persistent structural changes in the crystal lattice, has the greatest influence on the dissolution process. The first studies of radiation-kinetic effects on dissolution were instructive in this respect. Thus, Simnad and Smoluchovski[1] irradiated the oxide Fe_2O_3 with a stream of accelerated protons having an energy of 260 MeV, the density of the overall stream of protons reaching 10^{16} proton cm^{-2}. After irradiation, the oxide was dissolved in 1 N HCl solution and the liquid phase was analysed for iron by the periodic sampling method (Fig. 1). Fig. 1 shows that the irradiated oxide dissolves faster than the non-irradiated oxide. Such an increase in the rate of transfer of iron to the HCl solution can be explained by the appearance of a large number of bulk-phase defects (vacancies, displaced atoms, thermal peaks) as a result of the action of protons on the Fe_2O_3 crystal lattice. According to the authors[1], the characteristic change in the rate of dissolution as the latter proceeds is determined by two factors: the depletion of the surface in defects owing to their recombination, a greater ease of their diffusion in the surface region towards the interface (the loss of defects), and the gradual dissolution of the surface layer, which exposes the more damaged regions of Fe_2O_3. For this reason, an induction period is observed in the dissolution process.

The above publication was followed by a number of communications concerning the influence of irradiation with heavy particles on the rate of dissolution of purely ionic crystals in which not only the experimental results are described, but also an attempt is made to relate the observed effects to the formation of radiation-induced defects of a fully defined type.

A study has been made[10] of the dissolution of alkali metal halide crystals (NaCl, KCl, KBr) in their aqueous solutions after irradiation of the specimens with neutrons. Neutrons from an Ra–Be source were used. The most interesting result is the dependence of the quantity $v_{\mathrm{irr}}/v_{\mathrm{non\text{-}irr}}$ not only on irradiation but also on the duration of storage of the specimens after bombardment with neutrons before the start of dissolution (Fig. 2). The authors[10] suggest that, during the storage of the irradiated crystals (at 20°C), processes involving the thermal annealing of defects take place, which decreases the rate of dissolution. Furthermore, there is a possibility of the formation of new types of defects owing to the interaction of the primary defects, which leads to the stabilisation of the NaCl structure and a decrease of $v_{\mathrm{irr}}/v_{\mathrm{non\text{-}irr}}$. Unfortunately, the authors[10] did not put forward any hypothesis concerning the relations between v and a definite type of radiation-induced defect, and the irradiation conditions do not allow an exact determination of the integral neutron flux; no account is taken of the influence of γ-quanta accompanying the bombardment with neutrons either. However, in the above study a negative effect of neutron bombardment on the rate of dissolution was established for the first time and it was stated that the nature of the defects may have a decisive influence on the rate of transfer of the species from the solid to the solution. Further studies on these lines showed that the sensitivity of the rate of dissolution to irradiation with neutrons depends to a large extent on the type of crystal face. Anisotropy of the effect of radiation is characteristic of virtually all alkali metal halides. For example, the (100) face is most sensitive in KCl and NaCl crystals, while dissolution of the (110) and (111) faces proceeds at the same rate both before and after irradiation with neutrons (integral flux of 1 × 10^8 cm^{-2}).[10] One cannot rule out the possibility that this is associated with differences in the packing density of ions on the crystal faces, which leads, according to Naumov and Savintsev[12], to the following experimental relations between v on the crystal faces and the relative unsaturation of the solutions σ [σ is expressed as a fraction or as a percentage and is equal to $(c_0 - c_t)/c_0$)]:

$$v_{(110)} = R_1\sigma^{1.18}, \tag{3}$$

$$v_{(100)} = R_2\sigma^{1.65}, \tag{4}$$

where R_1 and R_2 are constants.

Interesting results for the influence of bulk-phase defects on the rate of dissolution were obtained by the above workers[12]. A layer 50 μm thick ("etching" with water) was removed before dissolution from KCl, NaCl, KBr, and KI crystals irradiated with the neutrons from an Ra–Be source and also with protons (E_{p} = 4.5 MeV, the intensity of the proton beam was 6 × 10^{10} proton $cm^{-2}s^{-1}$), which made it possible to disregard the macrodefects on the faces caused by bombardment with heavy particles. This was followed by the dissolution of the crystals. Neutron bombardment was accompanied by irradiation with γ-quanta having an energy of approximately 2 MeV, the crystals being exposed to a dose of 1.8×10^4 r. The energies of the protons and the neutrons were approximately the same and amounted to about 4 MeV. Experiments showed that, for large doses of heavy particles, the rate of dissolution, particularly under the conditions of low unsaturations, increases appreciably. The ratio $\nu_{irr}/\nu_{non\text{-}irr}$ decreases with increasing dilution of the solution (with increase of σ) and the influence of irradiation with heavy particles gradually becomes inappreciable. Irradiation with protons leads to a very marked increase in the rate of dissolution throughout the structure-sensitive region even for doses of the order of 10^{14} proton cm^{-2}.

Crystals such as those of LiF, the rate of dissolution of which is low, dissolve in pure distilled water ($\sigma \simeq \infty$) much more rapidly than the non-irradiated crystals, and a small change in the experimental temperature does not affect the nature of this relation. However, no hypothesis has been made concerning the relation between the change in ν_{irr} and the type of radiation-induced defects[12].

The increase in the rate of dissolution as a function of defects such as displaced atoms, dislocations, thermal peaks (wedges), etc. is more definite. For example, the density of dislocations in neutron-irradiated KCl crystals has been determined by an etching method[28] and it was found that immediately after irradiation the density of dislocations increases by a factor of 2.5 (to 7×10^5 cm^{-2}). Next, the number of dislocations decreases smoothly during storage at room temperature in accordance with the curve equivalent to the variation of $\nu_{irr}/\nu_{non\text{-}irr}$ for the same crystals (Fig. 2).

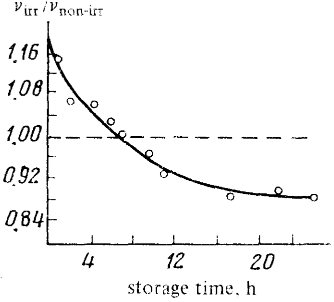

Figure 2. Dependence of the ratio of the rates of dissolution of irradiated and non-irradiated NaCl crystals on the duration of storage of the specimen at room temperature[10]. Solvent—25.85% solution of NaCl in water; integral neutron flux ~ 10^{11}–10^{12} neutron cm^{-2}.

An increase of ν_{irr} with increase of the integral flux of heavy particles was observed in all the systems investigated, and for equal fluxes the effect was greater for heavier particles. However, these conclusions are to a large extent qualitative, since neutron bombardment was always accompanied by intense γ-radiation, the influence of which was disregarded. Furthermore, even for equal integral fluxes and neutron and proton energies, the densities of the defects generated by these two types of radiation were different. Unfortunately, the concentration of even the total number of defects was not estimated. If this had been done, it would have been possible to compare the effects of neutrons and protons.

Naumov and coworkers[10–12] showed clearly for alkali metal halides that, under identical conditions, the greatest increase in the rate of dissolution is observed for crystals with the highest crystal lattice energy. This very important experimental fact can be used for the qualitative estimation of the influence of radiation on the dissolution process.

An increase in the rate of dissolution has been observed for the oxides Al_2O_3 and NiO and for mica[29] irradiated with accelerated krypton ions. The energy of the ions varied within a wide range (5–100 keV) and the integral fluxes were 5×10^{12} and 5×10^{13} cm^{-2}. The solvents were 3% HF for mica, NaOH solution for Al_2O_3, and concentrated HNO_3 for nickel oxide. The observed effect was attributed wholly to surface macrodefects on the irradiated specimens. This explanation appears to be quite likely, because krypton ions were absorbed by a thin layer of the test specimens, which made the surface amorphous, facilitating dissolution[29].

Table 1. Variation of the surface areas of solids as a result of exposure to neutrons and γ-quanta[30].

Substance	Type of radiation	Dose of No. of particles	Change in specific surface, % (the minus sign indicates a decrease and a plus sign indicates an increase)
TiO_2	γ	$1 \cdot 10^{22}$ eV g^{-1}	—15
C	neutrons	$7 \cdot 10^{19}$ neutron g^{-1}	0
α-Al_2O_3	neutrons	$2 \cdot 10^{18}$ »	0
γ-Al_2O_3	neutrons	$2 \cdot 10^{18}$ »	0
MgO	neutrons	$1 \cdot 10^{19}$ »	—25
SiO_2 (xerogel)	neutrons	$7 \cdot 10^{18}$ »	—3.3
SiO_2 (aerosil)	neutrons	$1 \cdot 10^{20}$ »	—69
BeO	neutrons	$4 \cdot 10^{18}$ »	+300
α-Al_2O_3	neutrons	$4 \cdot 10^{19}$ »	+300

It is not always possible to attribute the radiation-induced changes in the rate of dissolution solely to the effect of radiation on the structure and the surface area. For example, a study has been made[30] of the dissolution of oxides irradiated in a nuclear reactor in various media (H_2SO_4, HCl, NaOH). Measurements were made of the surface areas of the irradiated systems (Table 1) and it was found that, as a result of atomic displacements, thermal peaks, and sintering, the surface changes appreciably after irradiating the test specimens in the atomic reactor. Apart from all other factors, this process depends on the properties of the specimen: porosity, moisture content, degree of dispersion, and even the type of radiation-chemical reactions in the specimen. As a rule, the surface area decreased under the influence of irradiation with heavy particles. However, in these experiments[30] it was impossible to establish a clear relation between the changes in the rate of dissolution and the surface area.

Nevertheless in individual instances the role of the radiation-induced changes in the surface is shown quite clearly. Thus a study of the rate of transfer of uranium to the liquid phase when U_3O_8 irradiated with neutrons interacts with 0.1 *N* H_2SO_4 solution showed that the decisive factor in this process is the damage of the surface structure of the oxide[31], which causes complete surface amorphisation for integral fluxes in excess of 10^{17} neutron cm^{-3}.[32] Under these conditions, the rate of dissolution of the oxide increases. Fig. 3 shows that, for the doses investigated, there is an increase in the rate of transfer of uranium to the solution. There is a distinct difference in the behaviour of the irradiated and non-irradiated U_3O_8. One should note that the radiation-chemical decomposition of U_3O_8 under the influence of neutrons was scarcely observed, so that the solubility of this oxide in H_2SO_4 remained constant. This led to a gradual mutual approach of the dissolution curves for the irradiated and non-irradiated specimens, as the saturated solution was formed and the damaged surface layers dissolved. The time required for the equalisation of concentrations was approximately 10 days.

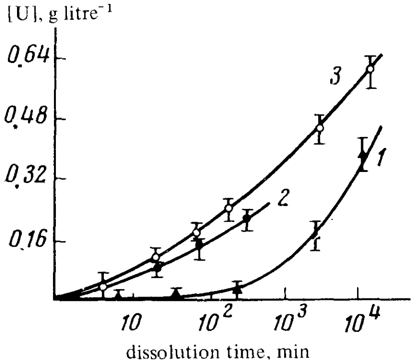

Figure 3. Kinetics of the transfer of uranium to the solution from neutron-irradiated U_3O_8: 1) non-irradiated U_3O_8; integral neutron flux (neutron cm^{-2}): 2) 1.2×10^{16}; 3) 1.2×10^{17}; temperature 30 ± 1°C.[31]

Table 2. The rate constants for the dissolution in water of various strontium sulphate specimens[33].

Specimen	$K_v = 10^7$ cm^{-2} s^{-1}
Non-irradiated	6.0
Irradiated with γ-quanta, dose 10^{20} eV g^{-1}	4.6
Irradiated by reactor radiation, 1×10^{18} neutron cm^{-2}	7.1
Radioactive crystals (50 mc of ^{35}S per gram of salt)	2.1

All the above examples involving crystalline compounds irradiated with neutrons are to some extent indefinite, since the contribution of the γ-quanta accompanying the neutron bombardment from any source was completely ignored in these experiments. In this respect the data of Gromov and Bespalova[33] throw some light on the problem, because they determined for the same object ($SrSO_4$ crystals) the influence of the mixed neutron and γ-radiation of the reactor, the separate effect of the γ-quanta from a cobalt source, and pure β-radiation (radioactive crystals) (Table 2). It was found that γ- and β-radiations retard the dissolution of strontium sulphate in water, while bombardment with neutrons accelerates it. Bearing in mind that neutrons and γ-quanta are active simultaneously in an atomic reactor, the acceleration of the dissolution process owing to the neutron flux alone is in fact much greater. One cannot rule out the possibility that neutrons, which cause very appreciable structural damage in the crystals, always promote dissolution. However, their influence may be masked and even completely suppressed by effects associated with the γ-radiation and the decrease of the surface area (see Jech and Kelly[29]), which was disregarded in the majority of investigations.

Summarising the discussion of the available experimental data, one may conclude that defects of the type of displaced atoms, dislocations, displacement zones, and interstitial atoms, which are very effectively generated on bombardment of the crystals with heavy particles, as a rule promote a more vigorous dissolution of the compounds.

IV. RELATION BETWEEN THE RADIATION-INDUCED DEFECTS AND THE DISSOLUTION OF COMPOUNDS IRRADIATED WITH γ-QUANTA AND ELECTRONS

In the first studies of the influence of X- and γ-rays and accelerated electrons on the kinetics of the dissolution of ionic crystals the extremely complex dependence of the rate of dissolution on the absorbed dose, on the degree of saturation of the liquid phase by the dissolved salt, and on the duration of storage of the irradiated compounds was already noted[7,9-12,28]. For example, it was found that a change in the concentration of the dissolved salt, even within narrow limits, has a significant influence on the ratio $v_{irr}/v_{non\text{-}irr}$ (Fig. 4). The data illustrated in Fig. 4 refer to the dissolution of NaCl crystals after exposure to X-rays[6]. According to the experimental conditions, the process occurred in the kinetic region of the dissolution reaction (Reynolds number $Re = 4000$). It is of interest to note that the ratio $v_{irr}/v_{non\text{-}irr}$ increases with increase of the NaCl concentration in solution, while the absolute difference between these rates diminishes, approaching zero as saturation is reached. The latter finding shows that the solubility of the irradiated crystals is equal to that of the non-irradiated crystals, i.e. radiation affects only the kinetic characteristics of the interphase interaction between the solid and the solvent.

In order to detect the change in solubility (c_0), which is a thermodynamic parameter, it is necessary to carry out experiments under adiabatic conditions; the energy evolved on dissolution (stored in the crystal during irradiation) then increases the temperature in the system, which affects c_0. Another procedure is evidently possible. The effect of radiation should then be strong enough to cause qualitative changes in the solid phase (the generation of chemical impurities, "fragments" of compounds, etc.), which might affect both the composition of the solution and c_0.

Berzina et al.[10] reached this conclusion in a study of the variation of the rate of dissolution of NaCl, KCl, and KBr crystals in aqueous solutions after irradiation on X-ray apparatus. In addition, they compared the changes in $v_{irr}/v_{non\text{-}irr}$ for the same specimens but different exposure doses (Fig. 5). Fig. 5 shows that, with increase of the radiation dose, the ratio of the linear rates of dissolution increases smoothly, other conditions being equal. Comparison of the data obtained for different salts also made it possible to establish the following empirical rule: if irradiation with X-rays leads to an increase of the rate of dissolution, the observed effect is greater the higher the energy of the crystal lattice of the given substance[10]. This rule holds in practice for a series of similar compounds (Table 3).

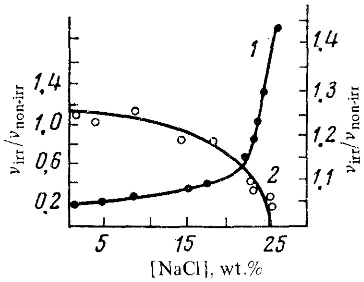

Figure 4. Dependence of the ratio (curve *1*) and the difference (curve *2*) of the linear rates of dissolution of irradiated and non-irradiated NaCl crystals on the salt concentration in solution; temperature 21°C; irradiation with X-rays[7].

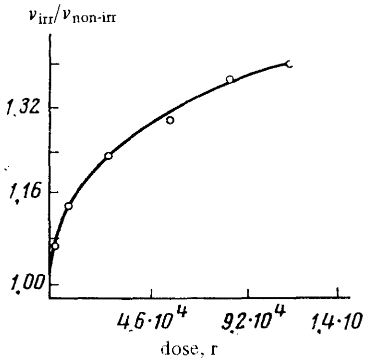

Figure 5. Dependence of the ratio of the rates of dissolution of X-irradiated and non-irradiated NaCl crystals on the dose[10]. NaCl concentration in solution used for the dissolution reaction 26 wt.%; temperature 21°C.

More detailed studies of the influence of X-rays (energy 8 keV) on the transfer of the ions of NaCl, KCl, etc., to the solution as a function of the degree of unsaturation σ have been made[11,12]. Anisotropy in the effect of radiation on different crystal faces was observed and it was established that irradiation not only accelerates, but also retards dissolution in certain ranges of σ. Thus, for a relative unsaturation of the solution less than 0.007, irradiation of an NaCl crystal leads to an increase in the rate of dissolution of the "100" face. When $\sigma > 0.007$, the rate of dissolution of this face is found to decrease, the maximum decrease corresponding to a dose close to 1×10^5 rad. With increase of the dose above 1.6×10^5 rad, the (100) face of the irradiated NaCl crystals then begins to dissolve once more at a higher rate than the non-irradiated face. For irradiated KCl crystals, the corresponding critical relative unsaturation resulting in a change in the sign of the effect of radiation on dissolution is $\sigma = 0.005$.

Table 3. Variation of the relative rates of dissolution on the (100) face of various X-irradiated alkali metal halide crystals (dose 1.2×10^5 rad).[12]

Crystal lattice energy, kcal mole^{-1}	Compound	Relative unsaturation σ					
		0.003	0.006	0.009	0.012	0.015	0.018
180	NaCl	1.65	1.10	0.90	0.90	0.90	0.93
164	KCl	1.15	0.97	0.83	0.78	0.76	0.82
158	KBr	1.06	0.99	1.00	1.00	1.00	1.00
149	KI	0.94	1.00	1.00	1.00	1.00	1.00

This complex relation between the rate of dissolution of the crystal face, the relative unsaturation of the solution, and the irradiation dose can be explained, according to the authors[11,12], by the fact that different structural defects in the crystal lattice affect the rate of dissolution of the irradiated compound to different extents (and sometimes in the opposite way). The above features are characteristic of the dissolution of the (100) face only, while along the other directions, (110) and (111), NaCl, KCl, and other alkali metal halide crystals are insensitive to the action of radiation[13].

The retardation of the transfer to the liquid phase of the ions of different substances irradiated with electrons, observed by many workers, is probably a fairly general phenomenon, which is frequently encountered. The same effect was noted for the dissolution of γ-irradiated uranium oxides U_3O_8 and UO_3 in sulphuric acid[31,34]. One cannot rule out the possibility that this type of action of γ-quanta can be accounted for by the radiation annealing of biographical defects owing to their recombination with the radiation-induced defects of opposite sign (for example, a vacancy and an atom in the interstices) generated under these conditions. The crystal then, as it were, becomes more perfect[35].

The first attempt to establish a relation between the change in the rate of dissolution of irradiated crystals and the concentration of defects of a particular type was apparently undertaken by Gromov and Bespalova[33], who investigated the influence of γ-quanta on the dissolution of strontium sulphate crystals in water. It was found that, with increase of the absorbed dose (regardless of the dose rate), the dissolution rate constant decreased smoothly to a constant value. For example, K_V for the non-irradiated salt was 6×10^{-7} cm^{-2} s^{-1}, while its minimum value (obtained for a dose of approximately 10^8 rad) was 3×10^{-7} cm^{-2} s^{-1}. Special experiments showed that electronic defects, i.e. holes and electrons localised at biographical defects, consisting mainly of the radical-ions SO_4^- and SO_3^- as well as e^-_{st} (the amount of SO_4^- exceeded that of SO_3^- almost by a factor of 10), are mainly formed in $SrSO_4$ under the influence of cobalt-60 γ-quanta[36-39]. The displacement of atoms and even more so of dislocations does not occur under these conditions. This facilitates the determination of the relation between the concentrations of definite radiation-induced defects and the rate of dissolution.

It was found that K_V decreases with increase in the concentration of SO_4^-, SO_3^-, and e_{st}^- (Fig. 6), i.e. there is a definite correlation between K_V and the number of electronic defects R. Without analysing the mechanism of the influence of the above defects on the transfer of Sr^{2+} and SO_4^{2-} ions to the liquid phase and solely on the basis of experimental data, the authors[33] represented the dissolution rate constant in the following form:

$$K_v = K_0 + K_{irr}, \tag{5}$$

where $K_{irr} = f(R)$, while K_0 is a constant. Bearing in mind that K_{irr} decreases exponentially with increase of the amount of R (Fig. 6), it is easy to obtain the final formula in the following form:

$$K_v = K_0 + K_1 \cdot \exp(-\alpha\,[R]), \tag{6}$$

where K_1 is a constant and α an empirical parameter with the dimensions particle^{-1}. When $[R] = 0$ (no irradiation), we have $K_V = K_0 + K_1$; when $[R] = [R]_\infty$ (maximum concentration of defects), we have $K_V \simeq K_0$. The values of K_1 and K_0 are determined from experimental data. The parameter α is found graphically from the slopes of the corresponding curves. Calculations have shown that the proposed formula describes satisfactorily the variation of K_V with the concentration of the radiation-induced defects of the electronic type.

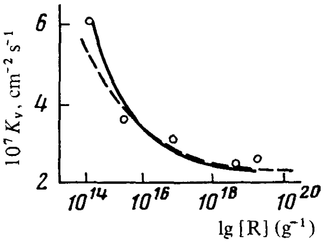

Figure 6. Dependence of the rate constant for the dissolution of $SrSO_4$ crystals on the concentration of defects (R) of the type SO_4^-, SO_3^-, and e_{st}^- in the crystal[33]. The dashed curve represents calculations by Eqn. (6).

Experiments with annealed $SrSO_4$ crystals provided satisfactory evidence for the relation between the decrease of K_V and the increase of the number of electronic defects. It was found that heat treatment at 400° C for 2 h restored the properties of the γ-irradiated specimens and that K_V for such specimens approached the value for the non-irradiated specimens[33]. In the course of this type of annealing, the SO_4^- and SO_3^- radical ions as well as e_{st}^- disappeared from the crystals, as shown by ESR.

The next step in refining the role of structural defects arising on irradiation was taken by Parkhaeva et al.[40] Crystals of natural (celestite) and synthetic strontium sulphate were subjected to the action of a stream of electrons with an energy of 3.5 MeV; the difference between these specimens was determined by impurities (thus the celestite contained approximately 1% of calcium, barium, magnesium, and potassium ions). Furthermore, the natural celestite crystals contained even before irradiation a fairly large number of SO_4^-, SO_3^-, and SO_2^- radical-ions, formed as a result of the β-decay of ^{87}Rb and the permanent level of background radiation. Thus the natural strontium sulphate had a fairly large number of biographical defects (an excess of dislocations cannot be ruled out either), which could serve as sites for the trapping of holes or electrons as well as sinks for the newly formed radiation-induced defects. As a result of irradiation with electrons having such large energies, displaced atoms should be formed in the $SrSO_4$ crystals in addition to the electronic defects and should be capable of stimulating the dissolution process. Indeed it was shown by ESR that in this instance the SO_3^-, SO_2^-, and SO_2^+ radical-ions as well as oxygen in the interstices are formed almost exclusively in the first stages of irradiation (up to 10^5 rad). SO_4^- radical-ions then gradually accumulate as well. Accordingly, the dissolution rate constant initially increases to a maximum and then gradually falls (Fig. 7).

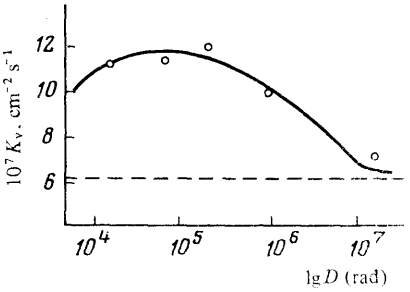

Figure 7. Variation of the rate constant for the dissolution of strontium sulphate as a function of the absorbed dose D after irradiation with fast electrons having an energy of 3.5 MeV. K_V for the non-irradiated crystals is represented by a dashed line[40].

Here there is competition between two types of defects—those which accelerate and those which retard dissolution. The gradual decrease of K_V is probably associated with the accumulation of point defects of the electronic type, in the present instance of SO_4^- and e_{st}^-, while the appearance of displaced atoms promotes dissolution. We may note that, with increase of electron energy to 5 MeV (the number of displaced atoms naturally increases under these conditions), the dissolution rate constant for a dose of ~ 10^5 rad increases approximately by a factor of 1.5 compared with K_V for specimens irradiated with electrons having energies of 3.5 MeV (also for a dose of 10^5 rad).

Extremely interesting results were obtained in a study[41] of the dissolution of γ-irradiated LiF crystals in distilled water containing iron ions. The authors showed that γ-radiation promotes the formation of two-dimensional defects in LiF crystals, which accelerated dissolution of the given salt on the (100) face. This was demonstrated by the appearance of double helices on the face undergoing dissolution, which did not occur in the absence of the radiation. The dissolution figures vanished almost completely and v correspondingly decreased after the annealing of the crystals in the course of 4 h at 550° C.

Summarising the data concerning the influence of γ-radiation and accelerated electrons on the dissolution of ionic crystals, certain conclusions may be drawn. Simple radiation-induced defects created by γ-quanta or accelerated electrons retard dissolution on irradiation under "milder" conditions (primary electronic or hole defects, for example, radical-ions, trapped electrons, etc.). The formation of displaced atoms, vacancies, and linear defects, which weaken the bonds in the crystal lattice and increase its free energy, promote the transfer of ions or molecules of the solid to the liquid phase. The formation of various associations of vacancies and displaced atoms as a result of postradiative processes can also retard dissolution. The sign of the effect of radiation on dissolution rate is therefore frequently reversed during the storage of such crystals.

V. THE INFLUENCE OF THE RADIATION-INDUCED CHARGING OF SOLIDS ON THE RATE OF THEIR DISSOLUTION

One cause of the retardation of the dissolution of irradiated crystals containing simple defects of the electronic type may be the radiation-induced charging of the dielectric crystals[40,42-47]. The appearance of an excess electric charge in irradiated solids was encountered for the first time after the discovery of radioactive elements and their accompanying radiations. Thus in 1900 Pierre and Marie Curie published the results of their experiments on the measurements of the charge of radium-containing barium salts[48]. This in fact has been used widely in the preparation of radioactive current sources (atomic batteries)[49-52].

In atomic batteries the source of radiation is usually surrounded by a weakly conducting medium—vacuum or a solid dielectric. In the latter case a space charge is gradually formed in the layer of the dielectric. The charging of dielectric materials is also observed, when they are irradiated with a stream of accelerated electrons and γ-quanta[51,53-65]. The concept of the charging of the bulk and surface of radioactive preparations has been used quite successfully recently to account for the characteristics of certain physicochemical processes involving the participation of radioactive solids[42,47,66-69].

The conditions for the formation of electric charges in irradiated materials have been fairly thoroughly investigated as a function of their dielectric properties[54,56,70-73]. A general theory of this phenomenon has been devised[51,52,59,61,73,74] and both empirical and theoretical formulae have been proposed, which make it possible to estimate both the magnitude of the radiation-stimulated charge[61,62] and the degree of polarisation of various specimens charged on irradiation[65,72]. A theory has been developed and measurements have been made of the accumulation of electric charges in radioactive crystals of inorganic salts[42,75-77].

Experiments have shown that, regardless of the mechanism of the formation of the radiation-induced charge and its distribution in the bulk of the solid, electric breakdown is observed under certain conditions, which is sometimes accompanied by the appearance of Lichtenberg figures[71,78-80]. This means that an electric field gradient, exceeding the breakdown potential, i.e. $E > 10^4-10^6$ V cm^{-1}, arises within the irradiated specimen. For example, when LiF crystals are irradiated with electrons having an energy of 1–2 MeV, tree-like channels—the tracks of electrical breakdown both during and after irradiation—develop within the crystal (for exposure doses of $1 \times 10^{15}-1 \times 10^{17}$ electron cm^{-2}). At the same time a large number of edge dislocations and particles of colloidal lithium appear along the channels and in the bulk of the crystal. All these features are superimposed on the radiation-induced defects[81]. The absence of electrical breakdown does not imply the absence of an excess of radiation-induced charge in dielectrics which have been irradiated with a stream of ionising particles; charging naturally leads to the appearance of bulk-phase polarisation, which persists for a long time after irradiation ceases.

Despite the fact that the charging of solids and the formation of a radiation-induced charge have been fairly thoroughly investigated, there has been virtually no systematic research concerning the influence of the electric field on the properties of solid specimens, the radiation-induced and radiation-chemical reactions in the latter, and also various heterogeneous processes. However, interesting information about the relation between the charge and properties of solids may be found in individual communications.

The formation of a radiation-induced charge has a marked influence on the kinetics of the formation and distribution of the radiation-induced defects in crystals[21,82], on the electron work function, and on the catalytic properties of solid oxide catalysts[66-68,83]. The influence of the electric field on the chemical and radiation-chemical processes in gases and liquids has been studied in detail (see Tal'roze's review[84]).

There are experimental data (admittedly only qualitative) concerning the appreciable influence of an external electric field and the charging of the solid phase on sorption phenomena in both liquid[47,85,86] and gaseous[68,69,87,88] phases. For example, anions[86] and negatively charged colloidal particles[85] are sorbed more effectively from solutions on positively charged crystals. Consequently the presence of an external electric field in a heterogeneous system, such as a solid–solvent system, or the appearance of excess charge at the interface on irradiation or polarisation alter appreciably the rates of processes involved in dissolution (sorption, crystallisation, orientation or disorientation of molecules at the interface, the rate of their migration in solution, etc.). All these factors make it possible to assume that the dissolution proper should also depend to a definite extent on the electric field in the system. The first experiments carried out on these lines confirmed the above hypothesis[45,46].

The theory of the dissolution of charged crystalline substances (dielectrics) has been most thoroughly developed at the present time. A possible relation between the charging of the crystals and the rate of their dissolution was postulated for the first time by Gromov and Bespalova[89] in a study of the dissolution of radioactive strontium sulphate crystals in water. Direct experiments then showed that NaCl, $SrSO_4$, etc. crystals, polarised by a permanent external electric field, dissolve more slowly than non-polarised compounds[45,90]. The polarisation of the solvent also has a definite influence; for this reason, the change in K_V depends in many respects on the ratio of the dielectric constants of the solid and liquid phases[90]. The intrinsic solubility of compounds is also very important (Fig. 8). Indeed, according to Fig. 8, with increase of the strength E of the field in which the crystals were polarised, K_V for celestite (the solubility of which is lowest among the substances investigated) decreases to the greatest extent. The relative decrease of K_V in series of salts of the same type (NaCl, LiF, NaF) is greater for lithium fluoride—a compound which is less soluble than NaF and which has a higher dielectric constant.

The observed changes in the rate of dissolution can be explained in terms of the general ideas of the dissolution theory and the hypothesis that K_V can be represented in the form of two multipliers, one of which does and one of which does not depend on the polarisation of the crystal[45]. Theoretical analysis of the influence of the charging of the crystals on the kinetics of their dissolution showed that the dissolution rate constant depends in a fairly complex manner on the dielectric properties of the crystal, the surrounding medium, the structure of the double layer at the crystal–solution interface, and the electric field strength within the crystal[45,91]. It has been established[45] that, with increase of the electric field strength in the crystal and for not unduly low bulk-phase concentrations in the liquid phase, K_V diminishes regardless of the sign of the charge localised in the crystal. The essential feature of this influence is that the polarised molecule (dipole) must perform additional work to overcome the electrostatic interaction forces on transfer from the charged specimen to the liquid phase.

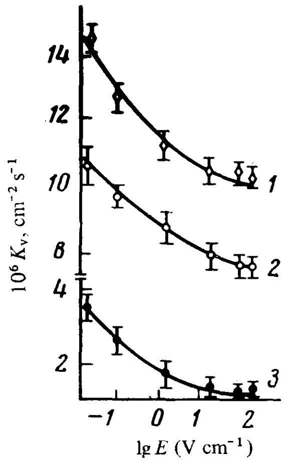

Figure 8. Variation of the rate constant for dissolution in water corresponding to different electric field strengths E (and hence different polarisations of the crystal)[90,91]: 1) NaF; 2) LiF; 3) $SrSO_4$.

Experiment showed that, in the dissolution of irradiated salts whose charge (and polarisation) is due to a non-uniform distribution in the bulk of the crystal of the carriers generated on irradiation, it is usually extremely difficult to isolate the influence of any one factor: charge, radiation-induced electronic defects, displaced atoms, or structural changes in the surface. This is because all the above consequences of the irradiation of the crystal are closely interrelated. However, we shall attempt to analyse the change in K_V for irradiated crystals which may be attributed to radiation-induced charging.

It has been established[36,38,39] that defects such as SO_4^-, SO_3^-, and e_{st}^- arise in $SrSO_4$ crystals irradiated with a stream of γ-quanta or accelerated electrons. At temperatures below −100° C for γ-irradiation or at room temperature for irradiation with electrons having an energy of approximately 1 MeV, only the SO_4^- radical-ions and thermalised electrons captured by traps are formed. Defects of the type of displaced atoms are not produced. Experiments with $SrSO_4$ crystals of this particular type were carried out by Parkhaeva et al.[40] The variation of the rate of dissolution of natural celestite ($SrSO_4$) irradiated with accelerated electrons having an energy of approximately 1 MeV is illustrated in Fig. 9.

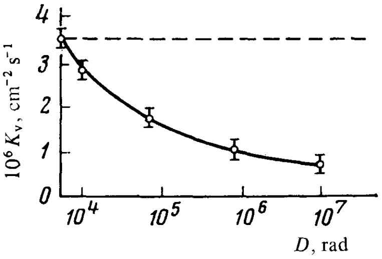

Figure 9. Dissolution of celestite single crystals in distilled water at 25° C after irradiation of the crystals with a stream of electrons having an energy of 3.5 MeV. The dashed line corresponds to non-irradiated crystals[40].

The experiments were performed as follows. The crystals were irradiated at 20–30° C (experiment showed that this entails the generation of the radiation-induced charge, SO_4^- radical-ions, and e_{st}^-) and were dissolved in distilled water at 25° C immediately after irradiation. Before dissolution, the outer layer of the crystal damaged by irradiation was removed by partial dissolution. Under these conditions, the changes in K_V could be attributed only to radiation-induced charging and the formation of electronic defects. Fig. 9 shows that celestite crystals freshly irradiated by electrons dissolve more slowly than the non-irradiated specimens. Evidently radiation-induced charging, the influence of which swamps that of radiation-induced effects, is of decisive importance in this instance. During the storage of crystals (for several months), the charge generated by irradiation partially leaked away (more precisely, the part of the charge not associated with the radiation-induced defects formed, whose concentration did not change during this period) and K_V increased somewhat, approaching the rate constant for the non-irradiated specimen. After thermal annealing, when all the defects disappeared, the properties of the irradiated and non-irradiated crystals were identical.

The results obtained for crystals of irradiated celestite can be explained satisfactorily by experiments with polarised specimens of the same mineral (Fig. 8, curve *3*)[90]: K_V decreases smoothly with increase of the strength of the electric field causing the polarisation of the crystal (cf. Figs. 8 and 9).

In another series of experiments, LiF crystals were irradiated with fast electrons[91]. The thickness of the LiF plates was chosen so that virtually all the electrons were absorbed in the specimen. In conformity with the theory of the radiation-induced charging and experimental determinations, the average excess space charge was negative. One of the irradiated crystals was placed in an electric field, the direction of which enhanced the radiation-induced polarisation. Others were placed in the field in such a way that its action promoted the depolarisation (the discharge) of the irradiated lithium fluoride. The results of these experiments are presented in Table 4, which shows that the smallest value of K_V is that of crystals in which the radiation-induced polarisation, caused by the non-uniformity of the distribution (and excess) of the charges, has been enhanced by the electric field. The decrease of polarisation as a result of the induced discharge of the irradiated LiF increases the rate of dissolution.

Table 4. Variation of the dissolution rate constant for electron-irradiated lithium fluoride crystals subjected to subsequent polarisation in an external 1500 V cm^{-1} electric field[91]*.

Experimental conditions	$10^6 K_V$, cm^{-2} s^{-1}
No field, crystal not irradiated	12.4
Field not applied to irradiated crystal	11.2
Electric field promotes discharge of irradiated crystal (depolarisation)	11.4
Electric field enhances polarisation of irradiated crystal	9.4

*The dose absorbed on irradiation amounted to 5 × 10^6 rad. Polarisation (depolarisation) time 48 h.

The experiments showed that on irradiation the influence of the radiation-induced charging can be observed in a pure form in certain cases. It is usually masked and partly swamped by the effect of radiation-induced defects. Evidently at least two opposed factors are manifested simultaneously in the irradiated compounds: the retardation of dissolution owing to the radiation-induced polarisation and the acceleration of the transfer of ions to the solution as a result of the formation of radiation-induced defects.

VI. RADIATION-CHEMICAL PROCESSES IN THE LIQUID PHASE AND DISSOLUTION

When the energy of ionising radiation is used to regulate dissolution processes, one can not only irradiate crystals before their interaction with the solvent, but an attempt can be made to act on the entire solvent–dissolved substance system. In this case the energy of the radiation is absorbed mainly by the liquid phase, because its amount is as a rule many times greater than that of the compound being dissolved. Furthermore, dissolution is usually rapid, and the radiation doses absorbed by the solid are much smaller than those which alter the rate of dissolution on preliminary irradiation of the crystals. Consequently the main radiation-induced processes occur in the liquid phase and the effect of radiation on dissolution is indirect—it is due to the interaction of the products of the radiolysis of the solvent with the solid phase.

Somewhat different conditions are possible in the dissolution of radioactive salts (the special case of dissolution directly during irradiation). It can be readily understood that here all the phenomena accompanying the dissolution of irradiated solids take place: radiation-induced charging, the accumulation of radiation-induced defects, breakdown of the structure of the surface, and radiolysis of the liquid phase. Bearing in mind that such salts are used in "atomic technology", the study of dissolution directly under irradiation is clearly of special interest.

The dissolution process has been studied directly in the field of γ-radiation, using the dissolution of the uranium oxides UO_2 and U_3O_8 in acid or alkaline media[92-94]; the rate of this process depends on the heterogeneous oxidation of uranium(IV) to uranium(VI)[95]. In the hydrometallurgical processing of uranium ores various oxidants (H_2O_2, O_2, MnO_2, etc.) are usually added to the liquid phase, which promotes the conversion of uranium(IV) into uranium(VI) and, in view of the higher rate of dissolution of uranium(VI) oxides compared with uranium(IV) oxides, this results in a more effective extraction of uranium from ores[96,97].

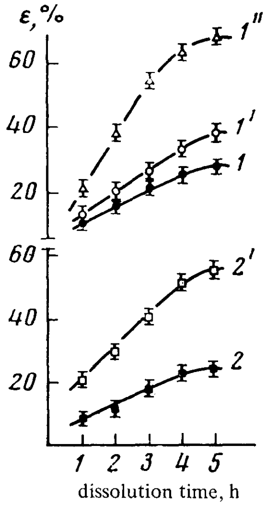

Figure 10. Variation of the degree of transfer of uranium ε to the liquid phase on dissolution of UO_2 and U_3O_8 in 0.1 N H_2SO_4: 1) U_3O_8, system not irradiated; 1′) and 2″) U_3O_8, system irradiated during dissolution using dose rates of 20 and 1.2 × 10^3 rad s^{-1} respectively; 2) UO_2, system not irradiated; 2′) UO_2, system γ-irradiated during dissolution using a dose rate of 1.2 × 10^3 rad s^{-1}.[92]

Experiments designed to investigate the dissolution process in the field of γ-radiation were performed with finely dispersed UO_2 and U_3O_8 powders, which were prepared by the usual methods[95]. Irradiation with ^{60}Co γ-rays was performed in air in open thermostatted vessels, with free access of air (aerated solutions). The dose rates used in the experiments were varied from 20 to 10^3

rad s^{-1}. The solvents consisted of 0.1 N H_2SO_4 and a carbonate solution (40 g $litre^{-1}$ of Na_2CO_3 and 30 g $litre^{-1}$ of $NaHCO_3$, pH ~ 10), which are used most frequently in the technology of the processing of uranium ores[96-98].

Fig. 10 presents the results of the determination of the degree of transfer of uranium (ϵ) to the solution for different dose rates. ϵ was determined from the expression

$$\varepsilon = ([U]_{soln.}/[U]_{solid}) \cdot 100, \qquad (7)$$

where $[U]_{soln}$ is the amount of uranium in the liquid phase at time t and $[U]_{solid}$ is the initial amount of uranium in the solid phase. Fig. 10 shows that, under the influence of γ-radiation, the degree of transfer of uranium to the liquid phase increases. At a dose rate of 1.2×10^3 rad s^{-1} ϵ increases approximately by a factor of 2.5 for U_3O_8 and 2.1 for UO_2. For higher radiation intensities, during prolonged dissolution (lasting more than 2 h), when the liquid phase was saturated with uranium and the consumption of H_2SO_4 began to have an effect, the increase in the rate of dissolution diminished. A similar relation between ϵ and the dose rate is characteristic of the dissolution of uranium oxides in the carbonate solution[93]. The influence of γ-radiation on the transfer of uranium to the solution was estimated in the above studies by comparing the rates of dissolution referred to unit surface area of the oxides.

The experiments showed that v is independent of the integral dose at least during the first hour, since the rate of dissolution of UO_2 remains constant in the course of γ-irradiation at a fixed dose rate. With increase of the dose rate, v steadily increases. The time interval corresponding to a constant value of v diminishes with increase of the dose rate, mainly owing to the gradual saturation of the liquid phase with uranium. The above features of the variation of v are characteristic of the dissolution of uranium oxides both in 0.1 N sulphuric acid and in the carbonate solution.

According to Gromov and coworkers[92,94], this shows that the decisive factor accelerating the transfer of uranium to the liquid phase (at least in the first stages of the dissolution process) is the interaction of the oxide undergoing dissolution with the radical products of the radiolysis of water, the concentration of which depends on the intensity of the radiation. This conclusion is confirmed also by experiments with radical acceptors, the addition of which to the solution sharply reduces the efficiency of γ-radiation. Thus the addition to the sulphuric acid solution of 1×10^{-4} M CH_3OH, which is an acceptor of OH radicals, decreased ϵ by a factor of 1.3 for a dose rate of approximately 400 rad s^{-1}.[94] Naturally, one cannot fully rule out the influence of the molecular products of the radiolysis of water, for example H_2O_2, etc., but their effect may be manifested only in later stages of the dissolution process when they have accumulated in sufficient amounts. At least during the first two hours, their influence may be disregarded.

Experiment showed that the increase of v with increasing dose rate (I) is not associated with the effect of radiation in the solid phase, since preliminary γ-irradiation of U_3O_8 or UO_2 *in vacuo* actually retards dissolution somewhat[31,34]. Consequently the acceleration of dissolution is caused by the oxidation of uranium(IV) to uranium(VI) by the products of the radiolysis of the liquid phase on the surface of the dissolving oxide. On this basis, the authors relate the rate of dissolution of uranium oxides to the intensity of γ-radiation. It was shown that, in the initial stages of the dissolution in both acid and carbonate media, the following relation holds[92]:

$$\lg v_I = \text{const} + {}^1\!/_2 \lg I, \qquad (8)$$

where v_I is the contribution to the overall rate of dissolution determined by the action of radiation. The main assumption in the derivation of the above formula is that the radical products of the radiolysis of water[99,100] namely OH and HO_2 in the sulphuric acid solution and O_2^- and CO_3^- in the carbonate solution, which are strong oxidants[101,102], play the main role in the dissolution process. These radical products oxidise uranium on the surfaces of the dissolving oxides to the hexavalent state, which accelerates the dissolution processes as a whole. In conformity with the adopted radiolysis mechanism, the steady-state concentration of the radical products of the liquid phase proved to be proportional to $I^{1/2}$, which in fact determines the final form of Eqn. (8).

The dependence of $\lg v_I$ on $\lg I$ in the dissolution of uranium oxides in sulphuric acid is illustrated in Fig. 11, which shows that the slope of the straight lines is 0.5 within the limits of experimental error, for both UO_2 and U_3O_8, in agreement with Eqn. (8). Deviations from the linear relation are observed for a dose rate of 1.2×10^3 rad s^{-1}, when the accumulated hydrogen peroxide (a molecular radiolysis product) probably accelerates the dissolution of the oxides. It was also noted that, after 2–3 h of dissolution, the experimental results ceased to agree with Eqn. (8). According to the authors[92] this is caused by the consumption of H_2SO_4 and the change in the surface area of dissolving oxides [in the derivation of Eqn. (8) the above parameters were assumed to be constant], which cannot be taken into account with adequate accuracy by the available methods. Eqn. (8) also holds fairly accurately in experiments involving the dissolution of UO_2 and U_3O_8 in the sodium carbonate solution[93,94]. The slope of the $\lg v_I$ – $\lg I$ straight lines for the carbonate medium is likewise 0.5, indicating the validity of the main assumptions made in the derivation of Eqn. (8).

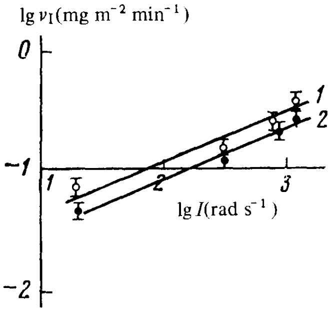

Figure 11. Dependence of $\lg v_I$ on the logarithm of the γ-radiation dose rate for UO_2 (line *1*) and U_3O_8 (line *2*) in the dissolution of the oxides in 0.1 N H_2SO_4. The values of v_I were calculated by Eqn. (8) for the range of dissolution times 0–60 min.[92,94]

Additional intensification of the dissolution of uranium dioxide can also be achieved as a result of the preliminary radiation-chemical solid-phase oxidation of uranium(IV) when the dry oxide is γ-irradiated in the presence of air. Thus X-ray diffraction showed that UO_2 acted upon by γ-quanta in air, for absorbed doses of approximately 10^8 rad, is converted into U_3O_8 to the extent of 20%. The radiation-induced oxidation of UO_2 in air probably proceeds via the following mechanism

$$UO_2 \xrightarrow{\gamma} (UO_2)^{*} + O_{2(air)} \text{ and } UO_2 \cdot mU_3O_8 \text{ or}$$
$$UO_2 + O_3 \xrightarrow{\gamma} n\,UO_2 \cdot m\,U_3O_8 \ . \tag{9}$$

The oxygen involved in the oxidation of UO_2 may be present in the dioxide itself (within pores and cracks) or can come from the surrounding medium.

The formation of uranium(VI) in uranium dioxide subjected to preliminary γ-irradiation affects also the rate of dissolution of UO_2, since the U(IV) → U(VI), transition limiting the rate of dissolution, takes place partly even in the solid phase under the influence of γ-irradiation[103-105].

Unfortunately the study of dissolution processes directly in the field of ionising radiation, which appears to be promising from the practical point of view, has so far been limited to the above system comprising uranium oxides and a sulphuric acid or carbonate solution[92-94,103-105].

Further studies on these lines will evidently yield much new and interesting practical and theoretical information.

VII. CONCLUSION

It follows from the data discussed that the rate of dissolution of irradiated solids is affected by many factors, which frequently act in opposition. Depending on the dissolution conditions, defects of only one type can be of decisive importance, while others play a passive role, although their concentration is in fact high.

The main effects of the radiation-kinetic phenomena in the dissolution process are associated with the formation of radiation-induced defects, a change in the structure of the surface, and the charging of the irradiated solid. However, their contribution is in many respects determined by the nature of the specific substance. For example, in the case of metals there is no point in taking into account the radiation-induced charging, since charges rapidly leak away and recombine with carriers of the opposite sign. This also applies to any non-metallic specimens whose intrinsic conductivity is more than 10^{-5} Ω^{-1} cm^{-1}.

The wide variety of the effects of radiation and their influence on the rate of dissolution creates certain difficulties in the study of the given phenomenon[43]. However, there are ways of reducing the influence of a particular change in structure on the dissolution process (Table 5). Table 5 shows that, in principle, it is possible to select conditions such that, after appropriate treatment of the irradiated compound, the effect of radiation on the dissolution process becomes insignificant.

A promising field for the utilisation of radiant energy in order to stimulate heterophase reactions (including dissolution reactions) involves the irradiation of the entire solid–solvent system. A necessary condition in this instance is the oxidation (or reduction) at the interface of the compound undergoing dissolution. If it limits the rate of dissolution, then ionising radiation may constitute an effective means of influencing the process as a whole.

Further development of studies on the practical utilisation of radiation-induced dissolution of solids depends on the solution of many theoretical and experimental problems.

Table 5. The influence of radiation-induced defects on the kinetics of the dissolution of solids[43].

Effect of radiation	Change in rate of dissolution	Method of reducing the influence of given effect
Displaced atoms and linear defects	acceleration	annealing
Trapped electrons or holes, radicals (electronic defects)	acceleration or retardation	annealing
Loosening of surface	acceleration	annealing, recrystallisation, dissolution of surface layers
Radiation-induced polishing of surface	retardation	annealing, prolonged storage of crystals before dissolution
Radiation-induced charging	retardation	
Dissolution of radiolysis products of solid	acceleration or retardation	annealing, change in liquid phase
Radiolysis products of liquid phase	acceleration (provided that dissolution process is accompanied by heterogeneous oxidation or reduction) have no influence on dissolution in the absence of oxidation (reduction) of solid phase	introduction of radical acceptors into liquid phase, experiments with non-oxidisable salts

1. The development of a theory of the influence of point defects of various types (primarily electronic) on the rate of dissolution.
2. The study of the effect of various impurities in the crystal lattice on the subsequent dissolution of the irradiated substances.
3. The study of the influence of a single definite type of defect on the values of K_V for various systems; the development of methods for suppressing (or forming) radiation-induced defects which are undesirable in the given specific instance. Evidently the use of the effect of light on the given system is extremely promising in this connection.
4. A wider employment of the effects of the irradiation of solid and liquid phases simultaneously; the selection of optimum conditions for the selective acceleration of the dissolution of complex systems under irradiation.

The development of these fields will not only extend and deepen our knowledge of the mechanisms of the dissolution of solids, but will undoubtedly make it possible to develop new practical methods for regulating heterophase processes.

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The Interaction of Carbon Dioxide with Transition Metal Complexes

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The reactions of transition metal compounds involving the formation of CO_2 complexes, reactions with insertion of CO_2 in transition metal-hydrogen and transition metal-carbon bonds, and homogeneous catalytic processes in which carbon dioxide behaves as a reactant or a modifying ligand are considered. A special section is devoted to reversible reactions accompanied by elimination of carbon dioxide under the influence of transition metal compounds.
The bibliography includes 306 references.

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I. INTRODUCTION

During the last five years there has been a considerable growth of interest in the reactions of carbon dioxide with transition metal compounds, primarily owing to the considerable advances made recently in the field of metal complex catalysis and in the first place in the activation of inert molecules (hydrogen, nitrogen, etc.) which leads to the expectation that catalytic processes involving carbon dioxide will also be carried out successfully. On the other hand, the CO_2 molecule may participate in catalytic processes also as a ligand capable of modifying the activity, selectivity, and specificity of catalysts. Evidently these two problems are most closely related to the synthesis and investigation of the transition metal complexes of carbon dioxide.

One may also note that the study of reactions involving systems based on transition metals is of considerable interest in view of the role that carbon dioxide plays in nature. Thus one may expect interesting results also when processes of this kind are simulated.

It has been believed for a long time that carbon dioxide reacts with transition metal compounds only in a "trivial" manner with formation of carbonates. However, recently many reactions have been discovered in which CO_2 behaves as a ligand or reacts to form new metal-C, C-H, or C-C bonds. This review is devoted to these new aspects of the carbon dioxide reactions.

II. PRINCIPAL PHYSICAL PROPERTIES AND STRUCTURE OF CARBON DIOXIDE

The carbon dioxide molecule is a linear triatomic molecule in which the carbon atom forms two equivalent bonds with oxygen atoms (of the σ and π types). According to spectroscopic data, the C=O bond length in the CO_2 molecule is 1.1615 Å,[1] which agrees with data obtained by electron diffraction[2].

There are fairly considerable discrepancies between calculated estimates of the heteropolarities of carbon dioxide: 75%[3,4], 10%[5,6], and virtually zero[7]. There are experimental literature data showing that the molecule has a permanent dipole moment (0.06×10^{-18} e.s.u.)[8], but, according to a later investigation[9], $\mu = 0$.

In the ground ${}^1\Sigma_g^+$ state ($D_{\infty h}$ symmetry group) sixteen electrons of the carbonyl molecule are distributed among the orbitals in the following manner: $(1\sigma_g)^2(1\sigma_u)^2(2\sigma_g)^2 . (2\sigma_u)^2(1\pi_u)^4(1\pi_g)^4$, where the least strongly bound π_g electrons are those of the lone electron pairs of the oxygen atom. Fig. 1 presents the energy level diagram for the CO_2 molecule; the energies of the atomic levels were taken from Siegbahn[10] and the experimental data (or, if these were lacking, calculated data) were taken from the review of Rabalais et al.[11] (Table 1). The data in Table 1 demonstrate a fairly good agreement between theory and experiment.

Table 1. Comparison of experimental and calculated lowest ionisation potentials (eV) of CO_2, CS_2, COS, allene, and keten.

Molecule	Experimental data (Refs.1,12-17)	MWH method (Ref.11)	Extended Hückel method (Ref.18)	CNDO method (Ref.19)	Hartree-Fock method (Ref.19)
O=C=O	13.78	14.05	17.20	14.55	14.81
	17.32	14.93	17.51	14.55	19.45
	18.08	17.68	18.14	16.83	2[illegible].23
	19.40	18.06	19.56	21.01	21.77
O=C=S	11.20	12.55	13.14	12.26	—
	15.08	13.67	14.67	13.81	—
	16.04	15.90	17.76	15.36	—
	17.96	16.50	18.40	19.32	—
S=C=S	10.09	11.33	12.24	11.33	—
	12.69	12.61	13.48	12.59	—
	14.47	14.44	14.18	13.28	—
	16.19	15.32	15.72	18.23	—
$H_2C=C=CH_2$	10.19	11.66	—	—	—
$H_2C=C=O$	9.60	11.49	—	—	—

Comparison of the energy level diagrams for the CO_2 molecule and the isoelectronic CS_2 and COS molecules (Fig. 2) shows that the highest occupied orbitals of the CO_2 molecule (π_g and π_u) lie appreciably below the corresponding CS_2 and COS orbitals[15].

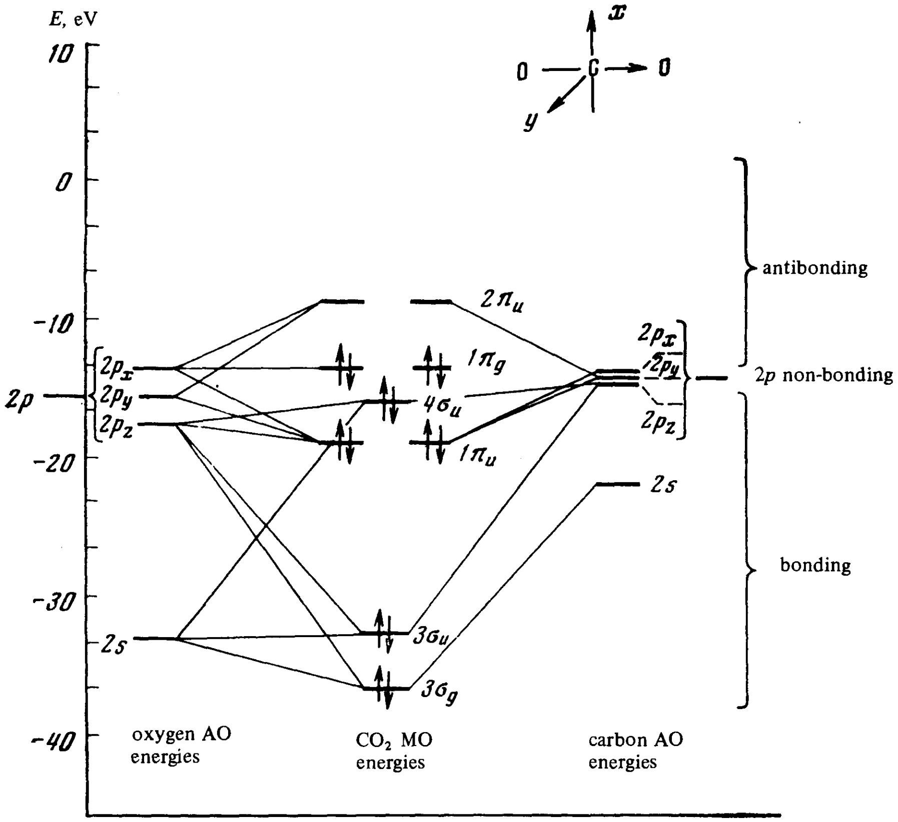


Figure 1. Molecular orbital diagram for the CO_2 molecule.

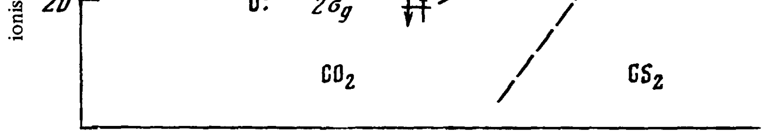


Figure 2. Electronic energy level diagram for CO_2 and CS_2 molecules according to photoelectron spectroscopic data.

Accordingly the ionisation potential of carbon dioxide (13.7 eV) is much higher than those of CS_2 (10.1 eV) and COS (11.2 eV). Thus the CO_2 molecule is a weaker electron donor than CS_2 or COS.

On the other hand, carbon dioxide has a low-lying $2\pi_u$ antibonding orbital, the position of which determines the electron affinity of the molecule [2.9 eV (Johnson and Albrecht[20]) or according to other (calculated) data ~ 3.8 eV (Buchel'nikova[21])]. These results appear to be rather too high. According to Berdnikov's calculated data[22], the electron affinity of CO_2 is ~ 0.5 eV, which agrees fairly well with experimental data[23,24].

The CO_2^+ species has been discussed[25-31] as a 15-electron species retaining its linearity in both the ground and excited states. The removal of one electron from the $1\pi_g$ orbital lengthens the C–O bond from 1.1615 Å ($^1\Sigma_g^+$) to

1.177Å ($^2\pi_g$) or 1.229 Å ($^2\pi_u$) [30] (Table 2). However, there are data showing that the anomalies in the infrared spectrum of CO_2^+ may be due to the bending of the excited molecule, the angle (168° ± 3°) corresponding to the distance r(CO) = 1.1830 ± 0.0004 Å.[32] The formation of the CO_2^{2+} ion has been observed by Newton and Sciamanna[33].

Table 2.

Molecule	Electronic state	Energy, eV	Bond length, Å	ν_1(symm.)	ν_2	ν_3(asymm.)
CO_2^+	$^2\Pi_u$	18.08	1.229	1131	560	1895
CO_2^+	$^2\Pi_g$	13.78	1.177	1280	632	2305
CO_2	$^1\Sigma_g^+$	0	1.163	1361	673	2379

The CO_2^- radical-ion, i.e. a species with a 17-electron configuration, has been obtained[34], in contrast to the extremely unstable CO_2^+ state, in a free form in a matrix on irradiation of sodium formate with high-energy γ-rays. Calculation of the valence angle by Coulson's method yielded 134°. According to the results of other workers[35, 36], the angle is 127 ± 8°. It is of interest that the O–C–O angle in sodium formate is 121.7° according to X-ray diffraction data[37].

It is noteworthy that Mulliken[4,38] and Walsh[39] predicted theoretically the possibility of the bending of the molecule on transition from the 16-electron linear configuration to the 17-electron configuration (i.e. from the $D_{\infty h}$ symmetry group to the C_{2v} symmetry group) (see also the review of Rabalais et al.[11]).

According to ESR data, the free electron in CO_2^- is localised at the carbon atom[20,36]. When the carbon atom is replaced by the ^{13}C isotope, the infrared band corresponding to the asymmetric vibrations of the carboxy-group shifts from 1671 cm^{-1} to 1626 cm^{-1} [36] (see also other data[20,40]).

The formation of the CO_2^- radical-ion has been postulated in a number of chemical and physicochemical studies: in the decomposition of oxalates in the presence of transition metals[41-43,44,45], in the electrochemical reduction of the CO_2 molecule[44,45], in electron transfer from a metallic surface on irradiation[46], in the reduction of carbon dioxide by amides[47] and alkali metal and alkaline earth metal amalgams[48-51], and in other reactions[52-56].

The most important physical properties of carbon dioxide are presented below:

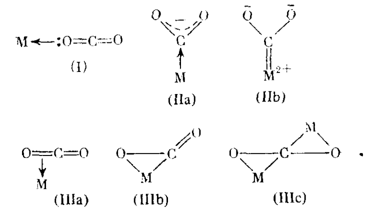
M.p. (5 atm)	-56.7°C
B.p. (sublimation at 1 atm)	-78.515°C
Density (at 0° and 1 atm)	1.9768 g litre^{-1}
Critical temperature	+31.3°C
Critical pressure	75.2 atm
Pressure corresponding to transition to liquid state (20°C)	58.46 atm
Heat of fusion (at 56.6°C)	2.24 kcal mole^{-1}
Standard free energy of formation	ΔF° = 94.260 kcal mole^{-1}
Standard entropy of formation	ΔS° = 51.011 cal mole^{-1} K^{-1}
Standard heat of formation	ΔH°_{298} = −94.08 kcal mole^{-1}
Temperature dependence of molar heat capacity (in the range 0–1400°C)	$C_p = 0.00326t + 0.00000079t^2 + 8.84$

III. TRANSITION METAL COMPLEXES OF CARBON DIOXIDE

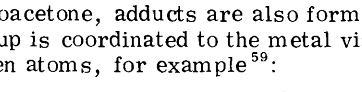
General consideration of the electron-donating and electron-accepting properties of carbon dioxide shows that there are several possibilities for the formation of complexes by CO_2 with transition metals. Complexes of the donor–acceptor type may be formed as a result of the transfer of the lone electron pair of the oxygen atom ($1\pi_g$ electrons) to the corresponding orbital of the metal atom (type I). In this case the transition metal plays the role of a Lewis acid. Interaction of this type is hindered by the comparatively high positive charge on the metal atom, the presence of low-lying vacant orbitals in the metal, and the presence of a free coordination site in the complex.

Another possibility may obtain as a result of the dative interaction involving the transfer of two electrons from the metal atom to the antibonding $2\pi_u$ orbital of carbon dioxide. In this case the CO_2 molecule is exhibiting electrophilic properties and a state of type IIa obtains. The transfer of two electrons from the metal atom to the antibonding orbitals of CO_2 may lead in the limiting case to the formation of a type IIb carbenoid complex. Clearly a low positive charge on the metal atom and the presence of electron-donating ligand in the complex will favour the formation of complexes of this type.

Finally the $1\pi_u$ orbital of the CO_2 molecule may interact with the corresponding vacant orbital of the metal with simultaneous transfer of the metal σ electrons to the vacant orbital of the CO_2 molecule which leads to the formation of a π-complex of type IIIa (or to the formation of a three-membered ring of type IIIb in the limiting case). Since the CO_2 molecule has two double bonds, an interesting possibility may arise when two metallic centres form a complex of type IIIb with a single carbon dioxide molecule:



It is remarkable that, when acetaldehyde acts on the ruthenium complex $(Ph_3P)_3RuCl_2$, a corresponding compound is formed in which the acyl group is coordinated to the metal atom by a π-type bond according to the authors[58]. When phosphine complexes of transition metals are acted upon by perfluoroacetone, adducts are also formed in which the carbonyl group is coordinated to the metal via both carbon and oxygen atoms, for example[59]:

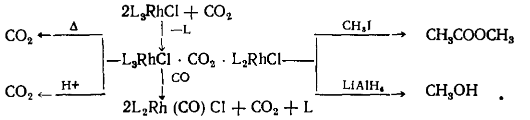


$$(Ph_3P)_4Pt + CF_3C(=O)CF_3 \rightarrow (Ph_3P)_2Pt\langle O{-}C(CF_3)_2 \rangle$$

The above structures naturally do not exhaust the entire wide variety of the possible types of complexes, particularly polynuclear complexes (complexes of this kind involve a combination of different types of complex formation reactions).

Since carbon dioxide is a less effective electron donor and a more effective electron acceptor than the isoelectronic CS_2 molecule, presumably complexes of type I are less typical for CO_2 and structures of type II and III are more typical (see the relevant reviews[60-64]. A fairly large number of CS_2 complexes are known[65,66], but the number of complexes with carbon dioxide which have been described is small.

The formation of complexes with carbon dioxide was observed for the first time for rhodium compounds[67]. Rhodium complexes of CO_2 are at present the most thoroughly investigated and we shall therefore begin our consideration of the available complexes by discussing the rhodium compounds. When carbon dioxide was allowed to interact with the complex L_3RhCl (where L = Ph_3P), a fairly stable adduct was obtained whose composition is $L_5Rh_2Cl_2.CO_2$ according to its chemical properties, the results of elemental analysis[67] and its infrared spectrum has an absorption band in the region of 1630 cm^{-1}. Chemical reactions also confirm the presence of coordinated carbon dioxide in the complex:



Carbon dioxide is evolved when the complex is acidified and pyrolysed. The formation of labelled carbon dioxide was demonstrated mass-spectrometrically in the thermal decomposition of the adduct formed in a $C^{18}O_2$ atmosphere[67]. Carbon dioxide is readily displaced from the complex by carbon monoxide.

It is interesting to note that the rhodium complex of carbon dioxide $L_5Rh_2(CO)_2(CO_2).C_6H_6$, obtained by an indirect procedure[68] (by oxidising the carbonyl group attached to the metal with oxygen), also has an asymmetric dinuclear structure according to molecular weight measurements. An interesting property of this complex is its ability to exchange the oxygen in a coordinated CO_2 molecule for dissolved molecular oxygen.

When the complex $[(Ph_3P)_2Rh(CO)]_2$ reacted with gaseous carbon dioxide at atmospheric pressure at room temperature in benzene, an asymmetric complex $(Ph_3P)_3Rh_2(CO)_2.(CO_2)_2.C_6H_6$ was again obtained[69,70]:

$$2\,[(Ph_3P)\,Rh\,(CO)_2] \xrightarrow{2Ph_3P} 2\,[(Ph_3P)_2Rh\,(CO)] \xrightarrow[-Ph_3P]{2CO_2} (Ph_3P)_3Rh_2\,(CO)_2\,(CO_2)_2\cdot C_6H_6\quad.$$

This complex is fairly stable and hardly loses carbon dioxide on exposure to air for several days. Carbon dioxide is evolved completely on pyrolysis and on treatment with acids or carbon monoxide. In the latter case the product is the complex $[(Ph_3P)Rh(CO)_2]_2$, i.e. the reaction is reversible also at atmospheric pressure:

$$2\,[(Ph_3P)Rh\,(CO)_2] \underset{2CO(-2CO_2;\;2Ph_3P)}{\overset{+2Ph_3P,\;2CO_2(-2CO)}{\rightleftarrows}} (Ph_3P)_3Rh_2\,(CO)_2\,(CO_2)_2\quad.$$

When the carbon dioxide is acted upon by oxygen, the familiar complex $(Ph_3P)_3Rh_2(CO)_2.CO_2$ is formed[68].

The infrared spectrum of the rhodium complex $(Ph_3P)_3.Rh_2(CO)_2(CO_2)_2$ contains, apart from the triphenylphosphine bands, two intense absorption bands in the region of 1600 cm^{-1} [ν(OCO)(asymm).] and 1355 cm^{-1} [ν(OCO)(symm.)] as well as a moderately intense band at 825 cm^{-1} [δ(OCO)]. When CO_2 in this complex is partly replaced by $^{13}CO_2$, the bands are split (Fig. 3). It is striking that the difference $\Delta = \nu(OCO)(assym.) - \nu(OCO)(symm.)$ amounts to 245 cm^{-1} for this complex, while $\Delta = 130$ cm^{-1} for the complex $L_3Rh_2(CO)_2.CO_2$ [ν(OCO)(asymm.) = 1498 cm^{-1}, ν(OCO)(symm.) = 1368, and δ(OCO) = 813 cm^{-1}]. This shows that in the rhodium complex with two CO_2 molecules there is an incomplete charge transfer from the metal atom to carbon dioxide, unlike the complex $L_3Rh_2(CO)_2.CO_2$ (cf. these data with those quoted by Peri[71]). The carbon dioxide in the $L_2Rh_2(CO)_2(CO_2)_2$ molecule is therefore retained less strongly, which is confirmed by chemical reactions. When olefins or oxygen are allowed to react with the complex $L_3Rh_2(CO)_2(CO_2)_2$, one carbon dioxide molecule is readily displaced with formation of the complex $L_3Rh_2(CO)_2.CO_2$.

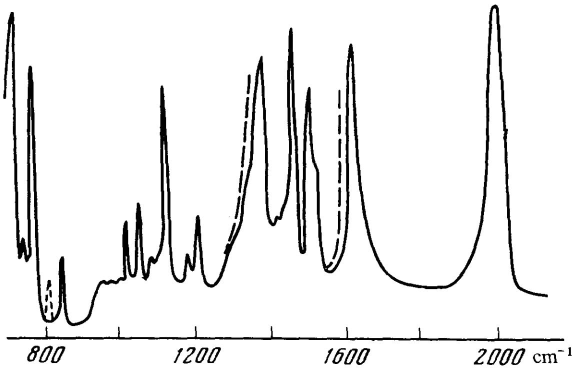
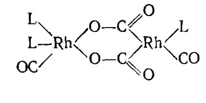
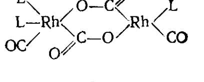


Figure 3. Infrared spectrum of the rhodium–carbon dioxide complex $(Ph_3P)_3Rh_2(CO)_2(CO_2)_2$ (the spectrum of the complex with $^{13}CO_2$ is indicated by dashed lines).

The complex $L_3Rh_2(CO)_2(CO_2)_2.C_6H_6$ is in all probability dinuclear, the two rhodium atoms being linked via two bent carbon dioxide molecules:





The appearance of three absorption bands in the spectrum of the coordinated carbon dioxide molecule instead of the two bands (2350 and 667 cm^{-1}) bands characteristic of the linear molecule (see Table 3) is associated with the bending of the CO_2 molecule on coordination.

Table 3. Vibration frequencies of the CO_2 molecule (cm^{-1}).

Molecule	State	ν_1	ν_2	ν_3	References
$^{12}CO_2$	gaseous	1343	667	2349	72
	solid (−190°C)	—	660	2344	73, 74
	aqueous solution	—	—	2342	75, 76
$^{13}CO_2$	gaseous	—	(649)	2284	75, 76
	solid (−190°C)	—	637	2280	73, 74
$^{14}CO_2$	gaseous	—	632	2226	75, 76

There are at present no X-ray diffraction data for carbon dioxide complexes of transition metals, but it is well known that the formation of complexes by carbon disulphide or allenes, which have linear molecules in the ground state, leads to the formation of compounds in which these molecules are bent. Thus it has been established by X-ray diffraction that the carbon disulphide molecule in the complexes $(Ph_3P)_2Pt.CS_2$ [77,78] and $(Ph_2P)_2Pd.CS_2$ [79] is bent (Fig. 4).

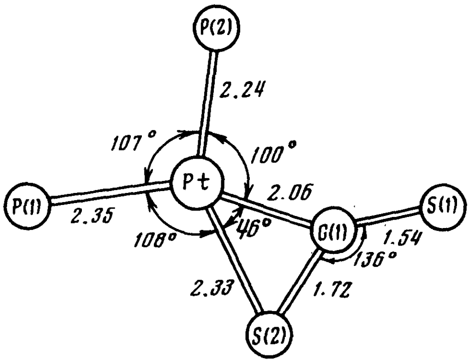
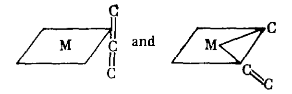


Figure 4. The structure of the platinum–carbon disulphide complex.

On the other hand, there are literature data showing that complexes of two types may be obtained with allene:



Thus in platinum, iron, and rhodium complexes[80-82] tetramethylallene is joined to the metal atom by a π-type linkage, while in the platinum complex $Pt(C_3H_4)(PPh_3)_2$ allene has a bent configuration[83].

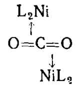
Apart from the absorption bands of physically adsorbed CO_2, the infrared spectra of chemisorbed carbon dioxide[71,84-99] contain other bands which the authors believe[71, 84-93] correspond to CO_2^- vibrations, the bands associated with the antisymmetric vibrations of the carboxy-group being located in the range 1570–1630 cm^{-1}, depending on the nature of the adsorbent, and those due to the symmetrical vibrations lying in the range 1320–1380 cm^{-1}.

The complexes $L_3Rh_2(CO)_2(CO_2).C_6H_6$ (2.83 μ_B) and $L_3Rh_2(CO)_2(CO_2)_2.C_6H_6$ (3.87 μ_B) proved to be paramagnetic[100] and their magnetic moments at room temperature (calculated per rhodium atom) are close to the spin-only value for two and three unpaired electrons respectively. It was shown in the same study that the anomalous paramagnetism of these complexes cannot be interpreted vigorously in terms of a model of the antiferromagnetic pair exchange in magnetically dilute dinuclear molecules.

The dimeric complex $(L_3RhH)_2.CO_2$, which Komiza and Yamomoto[101] obtained by passing carbon dioxide for a long time through a solution of the rhodium hydride $(Ph_3P)_4RhH$ in toluene, as well as the complex $L_5Rh_2Cl_2.CO_2$ [67] proved to be diamagnetic. The intense absorption band at 1460 cm^{-1} in the infrared spectrum of the resulting complex was attributed by the authors to the antisymmetric stretching vibrations of the OCO group, while the 1300 cm^{-1} band in the Raman spectrum was attributed to the symmetrical stretching vibrations of the same group. Carbon dioxide is evolved quantitatively from the complex on pyrolysis (at temperatures up to 200° C) and on acidification with sulphuric acid. On treatment with methyl iodide, carbon dioxide and methane are evolved.

The preparation of the complex $(Ph_3P)_3Co.CO_2$ in the form of a yellow compound inactive in air on treatment of $(Ph_3P)_3Co.N_2$ with carbon dioxide has been described[102]. When it is subjected to thermal decomposition or treated with sulphuric acid, the complex evolves CO_2. Its infrared spectrum has an absorption band in the region of 1890 cm^{-1}. The attempt[103] to obtain the analogous complex by treating the ethylene complex of cobalt $(Ph_2P)_3Co.(C_2H_4)$ with carbon dioxide at atmospheric or elevated pressure was unsuccessful.

The synthesis of the dinuclear nickel complex of carbon dioxide $\{[(C_6H_{11})_3P]_2Ni\}_2.CO_2$ by treating the corresponding nitrogenyl nickel complex with carbon dioxide has also been described[104]. The authors suggest that the metal atoms in this compound are coordinated via double bonds to the CO_2 molecule, which retains a linear structure:



$$\begin{array}{c} L_2Ni \\ \uparrow \\ O{=}C{=}O \\ \downarrow \\ NiL_2 \end{array}$$

An attempt has been made to obtain a platinum complex of carbon dioxide[105-107]. However, it was found that, when the complexes $(Ph_3P)_4Pt$ and $(Ph_3P)_3Pt$ react with CO_2 at an ordinary temperature and pressures up to 40 atm in the presence of traces of oxygen, carbonate complexes are formed (for further details, see below), while carefully purified carbon dioxide does not form stable products with platinum under these conditions, but the complex $(Ph_3P)_2Pt.CO_3$ is formed readily[108,109]. When the complex $(Ph_3P)_3Pt$ was treated with carefully purified carbon dioxide under pressure (40 atm) and a temperature in excess of 100° C, it was possible to obtain[61] a small yield of the compound $(Ph_3P)_2Pt.CO_2$, the infrared spectrum of which contains three intense absorption bands at 1640, 1370, and 1320 cm^{-1}. When the complex is pyrolysed, carbon dioxide is evolved.

Table 4. The energies of the $4f_{7/2}$ electrons of platinum ($L = Ph_3P$).

Compound	*E*, eV	Compound	*E*, eV
L_2PtCO_3	73.4	$L_2PtPhNCS$	73.1
L_2PtOCO_3	73.4	$L_2Pt(COPh)_2$	73.1
$L_2Pt(OOCH)_2$	73.4	L_2PtCS_2	73.0
$L_2Pt(OOCCH_3)_2$	73.7	$L_2Pt(COOMe)_2$	73.0
$L_2Pt(OOCEt)_2$	73.3	$L_2PtC_2H_4$	73.4
$L_2PtO_2\cdot(CH_3)_2CO$	73.3	$L_2Pt(PhC{\equiv}CPh)$	72.1
$L_2Pt\cdot O_2$	73.3	L_4Pt	71.7
L_2PtCO_2	73.2	Pt	71.3

A study of a series of platinum complexes with different types of ligand coordination (coordination to oxygen and carbon and coordination of the π-ligand type) by X-ray electron spectroscopy showed that the ability of the ligand to withdraw electrons from the metal atom decreases in the sequence (Table 4)[61]:

$$O_2 > CO_2 > CS_2 \sim PhNCS > COR > C_2H_4 > RC \equiv CR$$

The increase of the energy of the $4f_{7/2}$ electrons in the platinum complex of carbon dioxide relative to L_2PtCS_2 can be accounted for by the greater electronegativity of oxygen compared with sulphur.

Complexes of carbon dioxide and Group I metals (copper and silver) have also been obtained recently. When the complex $(Ph_3P)_2CuCH_3.CO_2$ is acted upon by carbon dioxide, the product is $(Ph_3P)_2CuOOCCH_3.CO_2$.[110] This complex is diamagnetic and evolves carbon dioxide on pyrolysis (above 200°C) and when treated with concentrated sulphuric acid. After the loss of carbon dioxide, the frequencies corresponding to the vibrations of the carboxylate group remain in the infrared spectrum, while the bands at 2620 (weak), 1600 (very strong), 1302 (very strong), 821 (moderately strong), and 648 (very weak) cm^{-1} disappear. On this basis, the authors[110] attribute the latter bands to the vibrations of coordinated carbon dioxide.

An interesting adduct was obtained when carbon dioxide was passed through a solution of copper complexes of ephedrine and its derivatives[111]. The authors investigated the ultraviolet spectra (λ = 250–260 nm) of these chelates in methanol solution and the visible spectra in benzene (Table 5). The study of the ultraviolet spectra showed that 1 : 1 adducts with carbon dioxide are formed in these solutions.

Table 5. Absorption spectra of copper(II) chelates in the visible region in benzene at 20°C.

Ligand in Cu^{II} chelate	λ^{*}_{max}, μm	ϵ^{*}, litre $mole^{-1}$ cm^{-1}	λ^{**}_{max}, μm	ϵ^{**}, litre $mole^{-1}$ cm^{-1}
(–)-Ephedrine	514	155	700	74
ψ-Ephedrine	500	121	700	82
N-Ethylnorephedrine	518	98	690	48
N-n-Butylnorephedrine	525	60***	660	41***

* $[Cu^{2+}]$ = 0.005 M.
** In the presence of CO_2.
*** Approximate value, because the chelate cannot be prepared in a crystalline form.

The thermodynamic functions for the complex-formation reaction between carbon dioxide and the complex Cu(ephedrine)$_2$ were determined[112] by gas–liquid chromatography (GLC): $\Delta G_{308} = -2.29 \pm 0.07$ kcal $mole^{-1}$, $\Delta H_{298-323} = 4.2 \pm 0.3$ kcal $mole^{-1}$; $\Delta S_{308} = -6.4 \pm 1.2$ kcal $mole^{-1}$ K^{-1}.

It is of interest that silver compounds also readily form stable complexes with carbon dioxide under mild conditions. Thus, when carbon dioxide is passed through a saturated solution of PhAg–$AgNO_3$ in ethanol at 0°C, a precipitate having the composition $C_7H_5O_2Ag_2$ is deposited[113]; its thermal decomposition results in the evolution of carbon dioxide. The infrared spectrum of this compound contains intense absorption bands in the region of 1496, 1326, and 828 cm^{-1} and moderately intense bands at 325, 290, and 280 cm^{-1}. The authors[113] concluded that a polymeric silver compound containing carbon dioxide is formed in this instance: $(C_6H_5AgCO_2Ag)_n$. An analogous complex was synthesised also from the corresponding *para*-substituted phenyl derivatives of silver.

Thus it is evident that a fairly large group of transition metals is capable of forming complexes with carbon dioxide. There is no doubt that the study of the complex formation reactions between carbon dioxide and transition metals constitutes an important branch of the chemistry of carbon dioxide and that the number of studies in this important field will increase in the immediate future and the problem of the structure of these compounds will be elucidated.

The problem of the isolation of fairly stable complexes with carbon dioxide was discussed above. However, in many cases the immediate formation of unstable CO_2 complexes in the course of various reactions has been postulated. There are literature data indicating the possibility of the formation of CO_2 complexes by the rupture of C–H bonds in transition metal formate complexes. On refluxing in benzene or on pyrolysis, the platinum formate complex $(Ph_3P)_2Pt(OOCH)_2$ decomposes into carbon monoxide and hydrogen[113]. On the other hand, when the solution contains the complex $(Ph_3P)_4Pt$, in which a C–H bond can be readily ruptured, the platinum formate complex decomposes with evolution of carbon dioxide[114], which has been attributed to the intermediate formation of a complex with CO_2, readily losing carbon dioxide via the mechanism

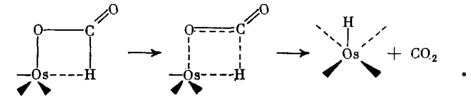
$$>\mathrm{PtOOCH} + \mathrm{Pt} \rightarrow \mathrm{PtOOCPt{-}H} \rightarrow CO_2 + \left\{>\mathrm{Pt{-}PtH}\right\} .$$

The intermediate formation of an unstable complex with carbon dioxide as a result of the intramolecular dissociation of the C–H bond in the formate group in all probability occurs in the reactions of ruthenium formate complexes[61,115]:

$$(Ph_3P)_3Ru\,(H)\,OOCH \rightleftarrows (Ph_3P)_3Ru\,(CO_2)\,H_2 \quad .$$

The formation of the ruthenium complex of carbon dioxide in one of the stages has been postulated for the reduction of unsaturated hydrocarbons with formic acid in the presence of the complex $(Ph_3P)_3Ru(H)Cl$ [116] and also for the decomposition of HCOOH in the presence of iridium complexes[117].

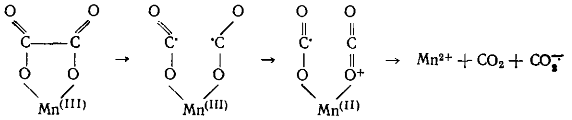
A complex with carbon dioxide is probably formed on thermal decomposition of osmium formate[118]:



When the cobalt formate complex $[Co^{III}(NH_3)_5OOCH]^{2+}$ is oxidised with manganese salts[119], the intermediate radical is fairly stable and reacts with another manganese species via the mechanism

$$\begin{aligned}[Co^{(III)}(NH_3)_5OOCH]^{2+} \xrightarrow{[MnO_4]^-;\ H+} \ & [Co\,(NH_3)_5OCO\,\cdot]^{2+} + HMnO_4 \\ & \downarrow \\ & [Co^{III}\,(NH_3)_5OH_2]^{3+} + CO_2 + [MnO_4]^- \quad .\end{aligned}$$

According to the results of other workers[120–123], the decomposition of oxalate in the presence of manganese salts also proceeds via the intermediate formation of a manganese complex of carbon dioxide:

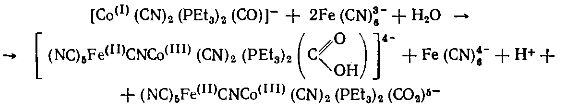


$$CO_2^{\cdot -} + Cl^{\cdot} \rightarrow CO_2 + Cl^- \quad .$$

(See also other investigations[124–127].)

In all probability analogous unstable complexes with carbon dioxide are formed in the decomposition of oxalic acid catalysed by copper[128,129], silver[130], mercury[131], and uranium[132] salts.

The intermediate formation of a cobalt complex of carbon dioxide was postulated[133] in a study of the mechanism of the oxidation of the $[Co^{I}(CN)_2(PEt_3)_2(CO)]^-$ complex with hexacyanoferrate(II) ions $Fe(CN)_6^{3-}$. Kinetic data confirm the occurrence of the equilibrium

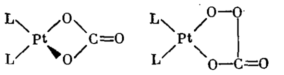


$$[Co^{(I)}(CN)_2(PEt_3)_2(CO)]^- + 2Fe(CN)_6^{3-} + H_2O \rightarrow$$
$$\rightarrow \left[(NC)_5Fe^{(II)}CNCo^{(III)}(CN)_2(PEt_3)_2\left(C\begin{smallmatrix}\diagup O\\ \diagdown OH\end{smallmatrix}\right)\right]^{4-} + Fe(CN)_6^{4-} + H^+ +$$
$$+ (NC)_5Fe^{(II)}CNCo^{(III)}(CN)_2(PEt_3)_2(CO_2)^{5-}$$

in solution. The authors[133] suggest that this mechanism operates also in the oxidation of carbon monoxide with oxygen catalysed by aquocobalamines[134-138].

IV. TRANSITION METAL CARBONATE COMPLEXES

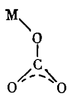
It is noteworthy that the widespread occurrence of the formation of transition metal carbonate complexes and their ability to evolve CO_2 on acidification of pyrolysis greatly hinder the identification of transition metal complexes of carbon dioxide or altogether prevent the formation of such complexes. As stated above, platinum and palladium complexes of the type $(Ph_3P)_4M$ (M = Pt or Pd) readily form carbonate complexes[105-109]. The possibility of the formation of a platinum carbonate complex on treatment of complexes of the type $(Ph_3P)_4Pt$ with carbon dioxide in the presence of traces of oxygen greatly depends on the nature of the coordinated ligand. Thus the carbonate complex is formed comparatively readily in the presence of the triphenylphosphine ligand, in the presence of the $(p\text{-tolyl})_3P$ ligand the yield of the corresponding complex is low, and in the presence of the $(p\text{-chlorophenyl})_3P$ ligand the complex is not formed at all. Carbonate complexes are formed when the complex $(Ph_3P)_2PtO_2$ reacts with carbon dioxide:



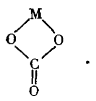
A platinum carbonate complex can be readily obtained when the complex *cis*-$(Ph_3P)_2PtCl_2$ is treated with Ag_2CO_3,[105] or when carbon monoxide is oxidised with oxygen coordinated to platinum[107]. Wilkinson and coworkers[107] made the following frequency assignments (cm^{-1}) in the infrared spectra of the compounds obtained:

Compound	$\nu(CO)$	$\nu(C-O)$(asymm.)	$\nu(C-O)$(symm.)	ν_{III}(symm.)	$\nu(O-O)$	$\nu(M-O)$	$\nu(M-P)$
L_2PtCO_3	1685 (s)	1185	980	815	—	363	409
L_2PtOCO_3	1678 (s)	1243	978	836	780	305	429

One may note that in general carbonates can behave as a monodentate [as in compounds (IV)] or bidentate [as in compounds (V)] ligand[139]:



(IV)



(V)

Nakamoto and coworkers[139] made a careful study of the infrared spectra of cobalt carbonate complexes and found that the C–O stretching vibrations in the monodentate carbonates give rise to absorption in the ranges 1360–1380 and 1450–1500 cm^{-1}, while the corresponding vibrations in the bidentate carbonates give rise to bands in the ranges 1260–1290 and 1590–1640 cm^{-1}, i.e. on the basis of infrared spectra it is virtually impossible to distinguish a transition metal complex of CO_2 from the carbonate complex. The structures of the carbonate and bicarbonate complexes have been discussed extensively[71,84-92] in connection with the study of the infrared spectra of chemisorbed carbon dioxide on metal oxides.

Like the ionic compound $CaCO_3$, where all the C–O bonds are equivalent, the platinum complex $(Ph_3P)_2PtCO_3$ has the structure[140] of a distorted square, also with equal C–O bond lengths.

The structure of the platinum peroxocarbonate complex[141] is probably analogous to that of the adduct $(Ph_3P)_2.PtO_2$.acetone. The oxygen in this complex is extremely reactive and readily oxidises triphenylphosphine with formation of a carbonate complex:

$$(Ph_3P)_2PtOCO_3 \xrightarrow{Ph_3P} (Ph_3P)_2PtCO_3 + Ph_3PO \quad .$$

There are also data demonstrating the ready formation of carbonate complexes when cobalt[103] and ruthenium[62] complexes react with carbon dioxide in the presence of traces of oxygen. In his attempt to obtain a molybdenum complex of carbon dioxide, Chatt synthesised a carbonate complex[142]. Carbonate complexes are readily formed also when an attempt is made to obtain a transition metal complex of carbon dioxide by an indirect method involving the oxidation of the carbon monoxide coordinated to the metal with molecular oxygen. An osmium carbonate complex has been obtained[143] by oxidising carbon monoxide with molecular oxygen:

$$(Ph_3P)_2OsCl(CO)NO \xrightarrow{O_2} (Ph_3P)_2OsCl(CO_3)NO \quad .$$

In discussing the mechanism of the formation of CO_2 when carbon monoxide and rhodium are oxidised with molecular oxygen, the authors[144] assume the formation of the unstable octahedral carbonate complex $[Rh^{III}(CO_3)(CO).Cl_3]^{2-}$, which readily gives off CO_2 in an acid medium.

The oxygen in a transition metal carbonate complex can be fairly reactive. Thus, when carbon monoxide was passed through a solution of the platinum carbonate complex $(Ph_3P)_2PtCO_3$, it was almost quantitatively oxidised[145] to CO_2, i.e. the reaction proceeded in accordance with the equation

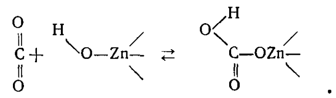
$$(Ph_3P)_2PtCO_3 + CO \rightarrow (Ph_3P)_2Pt + 2CO_2$$

Platinum carbonate complexes are used nowadays as catalysts for the synthesis of dimethylformamide from CO_2, H_2, and R_2NH and in the dimerisation of buta-1,3-diene to cyclo-octa-1,3,7-triene (see Sections V and VII respectively).

Ruthenium and rhodium bicarbonate complexes have been obtained recently[146,147] when the corresponding hydroxo-complexes were treated with carbon dioxide:

$$(Ph_3P)_2Rh(CO)OH + CO_2 \rightarrow (Ph_3P)_3Rh(CO)OCO_2H \quad ;$$
$$(Ph_3P)_4RuOH + CO_2 \rightarrow (Ph_3P)_4RuOCO_2H \quad .$$

These complexes are of some interest from the standpoint of the simulation of the action of a zinc-containing enzyme (carbonic anhydrase), which catalyses the reaction between carbon dioxide and water:



This type of analogy was drawn[148] in a study of the reaction of hydroxo-complexes of zinc with carbon dioxide. According to Riepe and Wang[149,150], in nature this process takes place in a hydrophobic cavity. There are data[151] showing that copper complexes also fulfill this function in nature.

V. INSERTION OF CARBON DIOXIDE IN A TRANSITION METAL–HYDROGEN BOND

Depending on the polarity of the transition metal–hydrogen bond, carbon dioxide can be inserted in the latter either with formation of formate complexes (normal insertion) or of metal-carboxylic acids (anomalous insertion):

$$O{=}C^{\delta+}{=}O^{\delta-} + M^{\delta+} - H^{\delta-} \rightarrow M{-}OOCH \ ;$$
$$O{=}C^{\delta+}{=}O^{\delta-} + M^{\delta-} - H^{\delta+} \rightarrow M{-}COOH \ .$$

The first reaction can serve as the basis of the catalytic reduction of CO_2 by molecular hydrogen with formation of formic acid derivatives, methanol, and other products. On the other hand, the reaction involving the formation of a metal-carboxylic acid can be of interest both for the synthesis of complexes of a new type and for the study of their properties, on the one hand, and for catalytic reactions involving the transfer of the carboxy-group to olefins and acetylenes, on the other.

It is noteworthy that, when CO_2 is inserted in a transition metal–hydrogen bond with formation of both a formate complex and a metal-carboxylic acid, the complex hydride may form a complex with a CO_2 molecule in the first stage, this being followed by insertion in the M–H bond. Thus, in a study of the kinetics of the analogous insertion of carbon disulphide in the transition metal–hydrogen bond in the complex $(Et_3P)_2Pt(H)Cl$, the authors [152] showed that the complex $(Et_3P)_2Pt(H)Cl.CS_2$ is formed in the first stage.

The insertion of carbon dioxide in a transition metal–hydrogen bond was observed for the first time [153] in relation to the cobalt complex $(Ph_3P)_3Co(N_2)H$. When CO_2 is passed through a solution of the complex, it is inserted in the Co–H bond with formation of the cobalt formate complex $(Ph_3P)_xCoOOCH$ as well as the complex $[(Ph_3P)_3.Co(CO)]_2$ resulting from the decarbonylation of the formate complex. The presence of the formate group was confirmed by the formation of methyl formate when the complex was treated with methyl iodide. The authors [153] noted the presence in the infrared spectrum of two broad absorption bands (at 1585 and 1370 cm^{-1}) corresponding to the asymmetrical and symmetrical vibrations of the COO^- groups.

A study of the reaction of carbon dioxide with the complexes $(Ph_3P)_3CoH_3$ and $(Ph_3P)_3Co(N_2)H$ established [154,155] the formation of a formate complex having infrared absorption bands at 1620 and 1300 cm^{-1}. In the presence of a deficiency of phosphine in solution, a mixture of a formate complex of unknown composition $(Ph_3P)_xCo(OOCH)$ and the decarbonylation product $(Ph_3P)_3Co(CO)H$ is formed. When the formate complex is acted upon by concentrated H_2SO_4, one mole of carbon monoxide and half a mole of H_2 are evolved per mole of the complex, while thermal decomposition results in the evolution mainly of carbon dioxide, hydrogen, and a small amount of carbon monoxide.

Special mention must be made of the reaction of sulphuric acid with transition metal formate complexes, which is a kind of test distinguishing metal formate complexes from carbon dioxide complexes (their infrared spectra are extremely similar) [155]. When formate complexes react with concentrated sulphuric acid, carbon monoxide is evolved, while carbon dioxide complexes evolve CO_2 under these conditions. When a cobalt formate complex is treated with dry HCl, formic acid is formed. The formation of a cobalt formate complex was confirmed in the above studies [154,155] also by synthesis on treating the corresponding hydride complex with formic acid.

When carbon dioxide was allowed to interact with the iron complexes $(Et_2PhP)_2FeH_4$ and $(Et_2PhP)_2Fe(N_2)H_2$, the iron formate complex $L_2Fe(OOCH)_2$ was obtained [156]. On treatment with ethyl bromide, the latter gives rise to the formate ester and on treatment with concentrated H_2SO_4 it decomposes, evolving CO:

$$L_2Fe\,(OOCH)_2 + 4C_2H_5Br \rightarrow FeBr_2 + 2HCOOC_2H_5 + 2LC_2H_5Br \ ;$$
$$L_2Fe\,(OOCH)_2 + H_2SO_4 \rightarrow FeSO_4 + 2H_2O + 2CO + 2L \ .$$

When carbon dioxide interacts with titanocene, a titanium formate complex is formed [157], in agreement with data [158] indicating the existence of the Ti–H bond in titanocene.

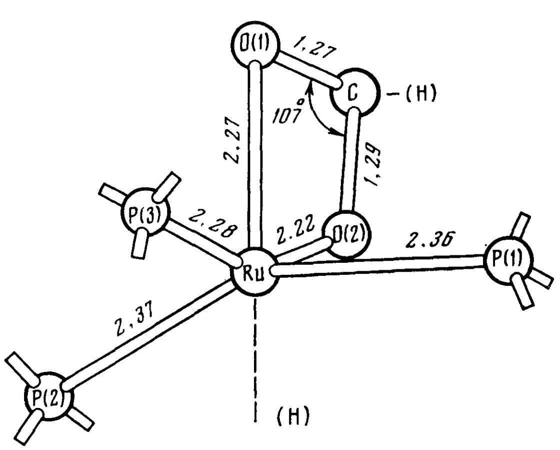
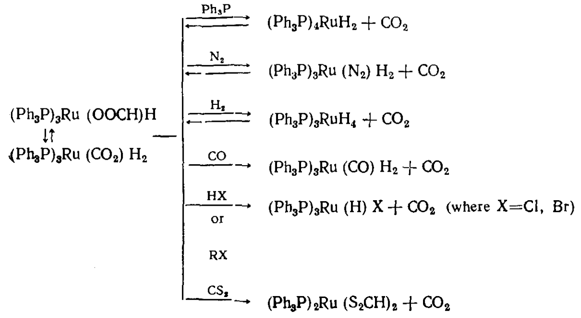


Figure 5. The structure of the ruthenium formate complex $(Ph_3P)_3Ru(H)OOCH$.

A ruthenium formate complex is formed [159,160] when carbon monoxide interacts with the complexes $(Ph_3P)_4.RuH_2$, $(Ph_3P)_3Ru(N_2)H_2$, and $(Ph_3P)_3RuH_4$. A compound having the composition $(Ph_3P)_3Ru(OOCH)H$ was obtained, its infrared spectrum containing, together with the absorption band due to the triphenylphosphine ligand and the band corresponding to the vibrations of the Ru–H bond (at 2010 cm^{-1}), also the following distinct bands: at 1565 (s.), 1420 (m.), 1370 (m.), 1355 (m.), 1340 (m.), 800 (s.), and 690 (v.s.) cm^{-1}. These bands are very close to those in the spectrum of the rhodium complex of CO_2 [67] and, on the other hand, virtually coincide with the frequencies of the ruthenium formate complex [161]. A detailed study of the infrared spectrum of the complex obtained by Kolomnikov and coworkers [159,160] showed that in the solid state it is a ruthenium formate complex. Thus, when carbon dioxide acts upon the deuterated complex $(Ph_3P)_3RuD_4$, the product is the complex $(Ph_3P)_3Ru(OOCD)D$, in the spectrum of which there are no 2910 (m.) and 2820 (m.) bands corresponding to the ν(C–H) vibrations and a band appears at 2150 cm^{-1} [the ν(C–D) band]. There is a corresponding disappearance of the $\nu(Ru{-}H) = 2010\ cm^{-1}$ band and its replacement by the $\nu(Ru{-}D) = 1450\ cm^{-1}$ band. The 1370 and 1355 cm^{-1} bands, which might be assigned to the deformation vibrations of the C–H bonds, are also missing from the infrared spectrum of the deuterated product. The residual bands are due to the vibrations of the OCO group.

X-Ray diffraction data[159,162] also confirm that in the crystalline state the compound obtained is a ruthenium formate complex in which hydride hydrogen is in the *trans*-position relative to the formate group (Fig. 5), i.e. the complex has a structure analogous to that of the known complex $(Ph_3P)_3Ru(H)OAc$.[163] However, when the formate complex was treated with methanol containing BF_3 and also with methyl iodide, the corresponding alkyl formates were not detected. It was found that the reactions of this complex[101,115,159,160], accompanied by the elimination of CO_2 under mild conditions, are unusual for the transition metal formate complexes described previously (see the mechanism below).

Carbon dioxide may be displaced from the ethylene complex or transferred to platinum when the complex interacts with $(Ph_3P)_2PtO_2$, forming the known carbonate $(Ph_3P)_2PtCO_3$.[61] It is specially noteworthy that the reactions of the ruthenium formate complex with triphenylphosphine, molecular nitrogen, and hydrogen are reversible (at atmospheric pressure and room temperature).



When the ruthenium formate complex reacts with carbon disulphide, the product is, as already mentioned, a dithioformate complex, which has the *cis*-structure according to X-ray diffraction data[164]. It has been shown[159] that on heating the formate complex $(Ph_3P)_3$.$Ru(OOCH)H$ is converted into the carbonylruthenium hydride complex $(Ph_3P)_3Ru(CO)H_2$, i.e. the formate fragment is decarbonylated. An analogous reaction involving the formation of a carbonyl derivative from a formate complex had been observed previously[155] for cobalt compounds. It has been shown quite recently[165] that under mild conditions CO_2 can serve as a source of CO for the synthesis of transition metal carbonyl complexes in the presence of reducing agents. Thus the complex $(Ph_3P)_3$.$RhCl$ interacts with CO_2 in the presence of the hydride $(EtO)_3SiH$ to form the complex $(Ph_3P)_2Rh(CO)Cl$ (in a quantitative yield)[165]. A carbonyl complex is formed in the presence of other silanes or aluminium hydrides. When the ruthenium complex $(Ph_3P)_3RuCl_2$ is introduced into the reaction, the product is the carbonyl complex $(Ph_3P)_3Ru(CO)Cl_2$. Presumably the silane aids to the transition metal complex in the first stage via an oxidative addition mechanism with formation of a transition metal–hydrogen bond and then CO_2 is inserted in this bond, forming a formate group, the decarbonylation of which leads to the formation of transition metal carbonyl complexes.

The formation of a formate fragment after the insertion of CO_2 in a cobalt–hydrogen bond in the complex was pointed out by Haynes et al.[166] On treatment with carbon dioxide, certain osmium, platinum, and iridium hydride complexes give rise to fairly unstable formate complexes which cannot be isolated in a pure state; however, their formation can be confirmed by treating the reaction product with methyl iodide and by isolating the formate ester[167].

The insertion of CO_2 in a transition metal–hydrogen bond can be used for the catalytic reduction of carbon dioxide. However, the process $CO_2 + H_2 \rightleftharpoons HCOOH$ is thermodynamically unfavourable under mild conditions. In order to displace the above equilibrium to the right, it is necessary to bind the formate fragment formed as a result of the reaction (for example, into a formamide or a formate ester) by adding the corresponding amine or alcohol to the reaction mixture.

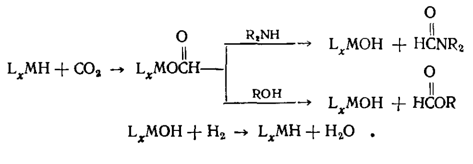
Thus it has been observed[166] that a whole series of transition metal complexes catalyse the formation of dimethylformamide in the reduction of carbon dioxide by molecular hydrogen in the presence of dimethylamine (Table 6). Other secondary amines, such as dipropylamine, pyrrolidine, and piperidine, also form rapidly the corresponding formamides. It proved impossible to extend the application of this reaction as far as the formation of *NN*-dimethylthioformamide by using carbon disulphide or carbon sulphide oxide in the presence of homogeneous hydrogenation catalysts.

Table 6. The reduction of CO_2 to dimethylformamide by molecular hydrogen in the presence of dimethylamine[166].

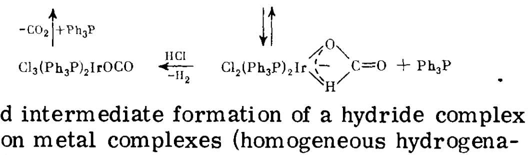
Catalyst	Catalyst concn., M	Me_2NH concn., M	Temp. *t*, °C	Yield, moles per mole of catalyst
$(diphos)_2CoH$	1.08	138	100	5
$(diphos)_2CoH$	0.05	131	125	1000
$(Ph_3P)_3RhCl$	0.3	122	100	43
$(Ph_3P)_3RhCl$	0.02	138	125	170
$(Ph_3P)_2Rh(CO)Cl$	0.38	144	100	1
$(Ph_3P)_2Ir(CO)Cl$	0.35	133	100	28
$(Ph_3P)_2Ir(CO)Cl$	0.2	138	125	1200
$(Ph_3P)_2PdCO_3$	0.79	159	100	120
$(Ph_3P)_2PtCO_3$	0.70	155	125	104
$(Ph_3P)_3Pt$	0.56	155	125	19
$(Ph_3P)_3RuCl_2$	0.39	132	125	8
$(Ph_3P)_3CuCl$	0.63	133	100	8

Formate esters have been obtained under similar conditions[167,168] using CH_3OH-BF_3 or $C_2H_5OH-BF_3$ mixtures as esterifying agents. Iridium and ruthenium complexes proved to be the most active catalysts. Although the formation of formaldehyde and methyl alcohol from carbon dioxide and hydrogen is thermodynamically favourable, these products were not detected in the reactions investigated[168]. Ruthenium complexes may catalyse the formation of formate esters also in the absence of BF_3. In a series of ruthenium complexes, the ruthenium(III) compound $(Ph_3P)_3RuCl_3$ proved to be the most active[65].

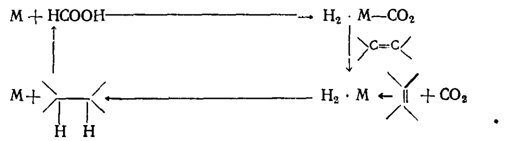
Formamides and formate esters are partly formed by the following mechanism in the reduction of carbon dioxide by molecular hydrogen in the presence of complex catalysts[167,168]:



The insertion of CO_2 in a transition metal–hydrogen bond and the reduction of carbon dioxide by molecular hydrogen in the presence of transition metal complexes are closely related to the reverse reaction—the decomposition of formic acid with evolution of carbon dioxide; this reaction is catalysed by various transition metal complexes[117,169–185]. It apparently proceeds via a stage involving the rupture of the C–H bond in the transition metal formate complex with transfer of hydrogen to the metal and the subsequent formation of a hydride complex with CO_2 as an intermediate. Thus it has been shown[117] that formic acid decomposes in the presence of an iridium catalyst via the following mechanism:



The suggested intermediate formation of a hydride complex when transition metal complexes (homogeneous hydrogenation catalysts) are acted upon by formic acid has been used for the catalytic transfer of hydrogen from formic acid to various organic substrates[184–193] (for further details, see Kolomnikov et al.[194]) via the mechanism



In the presence of catalytic amounts of $(Ph_3P)_3Ru(H)Cl$ in dimethylformamide formic acid reduces alk-1-enes rapidly and selectively to alkanes but does not reduce di- and tri-substituted alkenes (Table 7). It is noteworthy that under these conditions molecular hydrogen does not reduce olefins in the presence of the complex $(Ph_3P)_3$.$Ru(H)Cl$, i.e. the reduction of olefins by formic acid proceeds via intramolecular hydrogen transfer[192].

Table 7. The reduction of olefins by formic acid in the presence of $(Ph_3P)_3Ru(H)Cl$ in dimethylformamide (25°C, 3 h, HCOOH : olefin = 1 : 1).

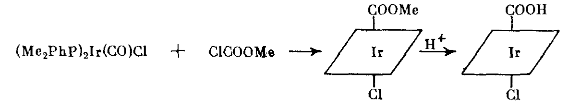
Compound	Reduction product	Yield, %
Oct-1-ene	n-Octane	100
Oct-4-ene	n-Octane	0
Hept-1-ene	n-Heptane	100
Hex-1-ene	n-Hexane	100
Methylcyclohexane	Methylcyclohexane	0
α-Methylstyrene	Cumene	0

Many other complexes of rhodium [L_3RhX, $L_2Rh(CO)X$, $L_3Rh(CO)H$, etc., where L = Ph_3P and X = Cl, Br, or I], iridium [$L_2Ir(CO)X$, $L_3Ir(CO)H$, L_3IrH_2Cl, etc.], ruthenium [L_3RuCl_2, L_4RuH_2, $L_3Ru(H)OAc$, and $L_3Ru(CO)(H)X$], platinum, and palladium, are also effective catalysts of the reduction of unsaturated compounds[186–191].

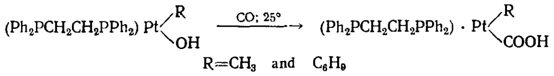
The hydrogenation[193] with formic acid of octatriene, formed in the course of the dimerisation of buta-1,3-diene by phosphine complexes of platinum and palladium of the type L_2MCl_2, has been observed:

Consequently the formation of formic acid from CO_2 and molecular hydrogen as well as the decomposition of formic acid catalysed by transition metal complexes proceed via the formation of formate complexes. Together with the synthesis of such compounds by subjecting transition metal hydride complexes to the action of CO_2 (see above), the formation of formates on reaction between formic acid and ruthenium and osmium[118,195–197], platinum[114], rhodium[198], and iridium[199] has been described. An unusual formate complex has been obtained for niobium[200,201]. According to X-ray diffraction data, the complex $\{[\pi\text{-}CpNbOOCH(OH)]_3O\}H$ contains oxohydroxo-groups apart from bridging bidentate formate groups. According to the authors[201], these groups are formed as a result of the decarbonylation of formic acid.

It may be supposed that transition metal complexes can interact with formic acid not only to form formate complexes but also with the initial rupture of the C–H bond and the formation of metal-carboxylic acids. Such cleavage of the C–H bond has been observed[202] in the reaction of formic acid with complexes of the type L_3IrCl_3 (where L = Me_2PhP, Et_2PhP, or Ph_3P), a complex with the Ir–COOH fragment being formed [ν(CO) = 1660, 1635, and 1610 cm^{-1} depending on the nature of the phosphine]. The properties of the complex proved similar to those of the iridium–carboxylic acid obtained previously by an indirect method[203] [ν(CO) = 1663 and ν(OH) = 3313 cm^{-1}].



A metal-carboxylic acid was obtained recently also from a platinum complex[204]:



$$(Ph_2PCH_2CH_2PPh_2)\,Pt\!\begin{smallmatrix}R\\OH\end{smallmatrix} \xrightarrow{CO;\ 25°} (Ph_2PCH_2CH_2PPh_2)\cdot Pt\!\begin{smallmatrix}R\\COOH\end{smallmatrix}$$

$$R{=}CH_3 \text{ and } C_6H_9$$

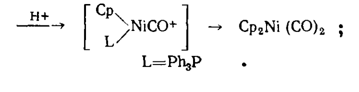
These compounds are stable in air in the solid state as well as in solution in methylene chloride or chloroform.

A metal-carboxylic acid is apparently formed also in the "anomalous" insertion of the CO_2 molecule in a Co–H bond when carbon dioxide interacts with the complex $[Ph_3P]_3Co(N_2)H$ in benzene solution. Methyl acetate is formed on treatment of the benzene solution with methyl iodide and then with a methanol solution of BF_3, as for iridium-carboxylic acids[103]:

$$[Co]H + CO_2 \rightarrow L_xCoCOOH \xrightarrow{MeI} MeCOOH \xrightarrow[-H_2O]{MeOH\cdot BF_3} MeCOOMe\ .$$

The formation of metal-carboxylic acids as intermediates has been suggested[205,206] in the oxidation of CO in the presence of mercury and silver salts.

The formation of cobalt-carboxylic acids[134–138], rhodium-carboxylic acids[207–210], and palladium-carboxylic acids[211,212] has been described. The formation of platinum-carboxylic acids has been suggested in the interaction of cationic carbonylphosphineplatinum complexes with water and in the hydrolysis of platinum-carboxylate esters[213,214]. The intermediate formation of a metal-carboxylic acid on treatment of an organonickel compound with carbon dioxide has been suggested in a recent study[215] undertaken to synthesise an organometallic analogue of a Grignard reagent:

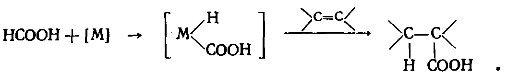


$$\begin{smallmatrix}Cp\\L\end{smallmatrix}\!NiBr + Mg \rightarrow \begin{smallmatrix}Cp\\L\end{smallmatrix}\!NiMgBr \rightarrow \left[\begin{smallmatrix}Cp\\L\end{smallmatrix}\!Ni{-}COOMgBr\right] \rightarrow \xrightarrow{H+} \left[\begin{smallmatrix}Cp\\L\end{smallmatrix}\!NiCO^+\right] \rightarrow Cp_2Ni\,(CO)_2\ ;$$

$$L{=}Ph_3P\ .$$

A study of the reaction of carbon dioxide with NaCo.(Salen)$_2$ (where Salen is *NN*′-bis-salicylethylenediamine) showed[216] that the formation of the sodium salt of cobalt-carboxylic acid is reversible. The absorption bands of the coordinated carbon dioxide in this compound are in the region of 1680, 1278, and 1213 cm^{-1}.

Presumably the formation of metal-carboxylic acids is an intermediate stage in the catalytic transfer of the COOH group from formic acid to unsaturated compounds via transition metal complexes:



$$\mathrm{HCOOH} + [M] \rightarrow \left[M\begin{smallmatrix} H \\ COOH \end{smallmatrix} \right] \xrightarrow{>C=C<} >\underset{H}{C}-\underset{COOH}{C}< \ .$$

This reaction, involving the addition of formic acid to unsaturated compounds, leads to the formation of higher carboxylic acids[61,217] (Table 8).

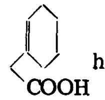
It is of interest that a platinum complex of the type (diphos)Pt  has been obtained recently[204]. Evidently this compound simulates to some extent the intermediate in the addition of the carboxylate group to an unsaturated compound.

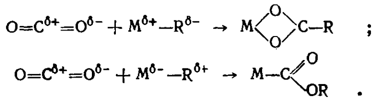
Table 8. The addition of formic acid to cyclohexene in the presence of metal complexes (100° C, 8 h, HCOOH : olefin = 1 : 1).

Catalyst	Solvent	Conversion, %	Yield of cyclohexanecarboxylic acid, moles per mole of catalyst
$(Ph_3P)_3RhCl$	—	7.0	39.0
$(Ph_2PH)_3RhCl$	—	7.3	42.0
$(Ph_3P)_2Ir(CO)Cl$	—	8.7	32.0
$RuCl_3$	DMF	2.1	3.0
H_2PtCl_6	Ethanol	7.0	18.0

VI. INSERTION OF CARBON DIOXIDE IN A TRANSITION METAL–CARBON BOND

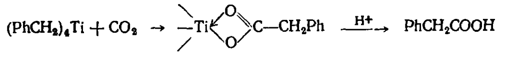
The insertion of CO$_2$ in an M–C bond is well known and has been used successfully in the chemistry of non-transition metals[62]. However, reports of the insertion of gaseous CO$_2$ in a transition metal–carbon bond have appeared only very recently. Furthermore, such reactions are of great interest because they lead to the possibility of introducing CO$_2$ into catalytic and synthetic processes.

As in the reaction where CO$_2$ is inserted in a transition metal–hydrogen bond (see the previous Section), when it is inserted in a transition metal–carbon bond, two pathways may obtain—the "normal" pathway with formation of carboxylate complexes and the "anomalous" pathway with formation of metal-carboxylate esters:



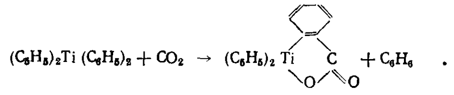
$$O{=}C^{\delta+}{=}O^{\delta-} + M^{\delta-}{-}R^{\delta+} \rightarrow M{-}C\begin{smallmatrix} {/\!\!/}O \\ \diagdown OR \end{smallmatrix} \ .$$

The normal insertion of CO$_2$ in transition metal–carbon σ bonds has been described for titanium, zirconium, zinc, cobalt, rhodium, and copper compounds. Thus it has been shown[218] that carbon dioxide is inserted in a titanium (zirconium)–carbon bond with formation of the corresponding acids after acidification. Organometallic compounds absorb up to two moles of CO$_2$ per mole of the complex and the reaction involving zirconium compounds proceeds at a rate higher by two orders of magnitude than for titanium compounds owing to the greater polarity of the zirconium–carbon bond. The authors[218] did not isolate the organometallic derivative from the reaction mixture but after hydrolysis yielded phenylacetic acid and triphenylcarbinol in equimolar amounts. The formation of phenylacetic acid is consistent with the mechanism of the "normal" insertion of CO$_2$ in a transition metal–carbon σ bond:



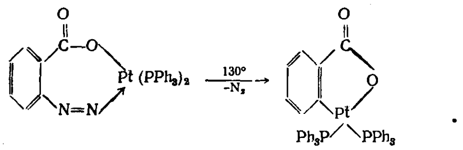
The insertion of CO$_2$ in a methyl–titanium σ bond has been observed[157] also in the reaction of dimethyltitanocene with CO$_2$ to form the —TiOOCCH$_3$ fragment. The infrared spectrum of the reaction products is identical with that of the known titanocene diacetate[219–221]. The presence of the acetate group has also been confirmed by the fact that, when the reaction product is esterified with methanol, methyl acetate is formed.

A fairly unexpected result was obtained in a study of the insertion of CO$_2$ in a titanium–carbon σ bond in diphenyltitanocene. At 80° C (this constitutes the condition for the thermal decomposition of diphenyltitanocene) and atmospheric pressure the reaction leads to the formation of a stable compound containing a five-membered ring incorporating a titanium atom, two *o*-carbon atoms of the benzene ring, and a CO$_2$ molecule[157,222,223]:



The compound obtained is diamagnetic. Its infrared spectrum contains a series of distinct bands together with the absorption bands of the phenyl and cyclopentadienyl groups: at 1660 (v.s.), 1620 (s.), 1280 (v.s.), 1130 (s.), and 880 (s.) cm^{-1}. A very intense band at 1660 cm^{-1} apparently corresponds to the ν(OCO) vibration. The frequency of this vibration is intermediate between the corresponding values for the ionised and unionised carboxy-groups. It is also of interest that in the region of the infrared spectrum characterising substitution of the benzene ring there are two bands: at 690 (m.) and 735 (s.) cm^{-1}; the region is as a rule uncharacteristic of 1,2-disubstitution.

It is noteworthy that an analogous infrared spectrum has been observed for a cyclic platinum complex obtained by the reaction of azocarboxylic acid followed by the elimination of nitrogen on heating [ν(OCO) = 1646 and 1620 cm^{-1}; ν(OCO) = 1305 and 1298 cm^{-1}][224,225]:



(VI)

On the other hand, the infrared spectrum of a cyclic organotitanium compound differs from that of Cp$_2$Ti(OOCPh)$_2$ (Cp = C$_5$H$_5$) [ν(OCO)(asymm.) = 1610 cm^{-1}; ν(OCO) (symm.) = 1410 cm^{-1}][226] or the paramagnetic complex $Cp_2Ti(OOCPh)$[227].

Behaviour unusual for *o*-substitution has been observed in the Raman spectrum of compound (VI). Whereas the Raman spectrum of dicyclopentadienyldiphenyltitanium, recorded for comparison, has the usual monosubstitution lines at 620, 994 (v.s.), and 1006 (w.) cm^{-1}, the spectrum of compound (VI) has no 620 cm^{-1} line, but there are two new lines: at 1011 (s.) and 1027 (w.) cm^{-1}. Similar spectroscopic behaviour has been observed for certain *o*-substituted benzenes, but the above intensity ratios are unusual for *o*-substitution.

X-Ray diffraction data[222,223] have shown that the Ti–C σ bond in this compound is appreciably shorter (2.20 Å) than in dicyclopentadienyldiphenyltitanium (2.27 Å) (Fig. 6). This finding is fully consistent both with the thermal stability of the bond (the substance does not decompose on heating to 190° C, in contrast to Cp_2TiPh_2) and with the chemical stability of the compound, in contrast to the titanium benzoate complexes with the usual coordination, which were mentioned above.

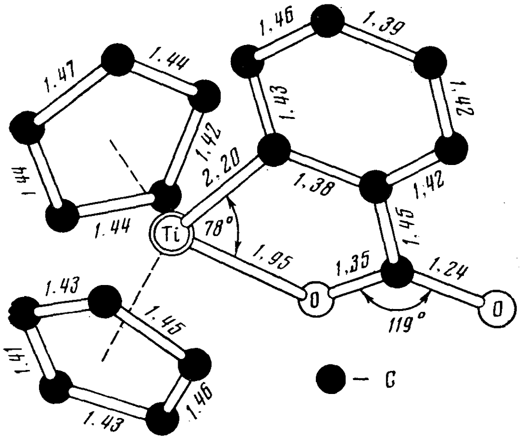
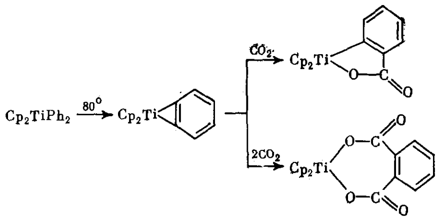


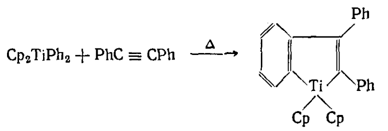
Figure 6. The structure of the complex $Cp_2TiOOCC_6H_4$.

Other chemical reactions also agree with the proposed structure of the cyclic compound. Thus, on treatment with methanol containing BF_3 (at 100° C), methyl benzoate is formed, while treatment of the compound with methyliodide leads to the formation of a mixture of ethyl esters of benzoic and *o*-toluic acids. When the organotitanium complex is heated for a long time with hydrochloric acid, the products are benzoic acid and titanocene dichloride. It is noteworthy that the reaction of CO_2 with diphenyltitanocene takes place partly with insertion of a second carbon dioxide molecule in a titanium–carbon σ bond and the formation of a phthalate complex.

All the data obtained are consistent with the hypothesis[228] that the decomposition of diphenyltitanocene proceeds via the intermediate formation of a titanium–dehydrobenzene complex:



It is of interest that, when diphenyltitanocene interacts with tolane under the thermal decomposition conditions, a cyclic compound is also formed[229]:



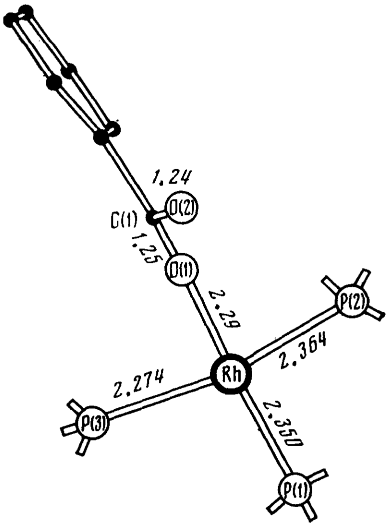
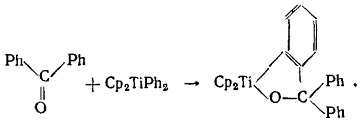


Figure 7. The structure of the rhodium benzoate complex $(Ph_3P)_3RhOOCC_6H_5$.

Ketones and isocyanates (analogues of CO_2) are similarly inserted in a carbon–titanium bond[230]. For example, when benzophenone reacts with diphenyltitanocene, a cyclic compound is formed:



Its hydrolysis leads to the formation of triphenylmethanol.

Carbon dioxide is readily inserted in a copper–carbon σ bond in the complex $(Ph_3P)_2CuCH_3$ with formation of the carboxylate complex $(Ph_3P)_2Cu(OOCCH_3)CO_2$ (see also Section IV) in tetrahydrofuran (THF) at –40° C and atmospheric pressure[110]. The NMR spectrum of the product (in pyridine) has a signal corresponding to the methyl of the acetate group (τ = 7.37 p.p.m.) but no signal due to the methyl group of the initial complex (τ = 10.3 p.p.m.). When the complex is treated with hydrochloric acid, acetic acid is produced:

$$CH_3COOCu\,(PPh_3)_2 \xrightarrow{3HCl} CH_3COOH + CuCl + PPh_3 \cdot HCl\ .$$

On the other hand, treatment with alkyl iodides results in the formation of the corresponding esters[110]:

$$CH_3COOCu\,(PPh_3)_2 \begin{cases} \xrightarrow{CH_3I} CH_3COOCH_3 \\ \xrightarrow{C_2H_5I} CH_3COOC_2H_5\ . \end{cases}$$

The same complex may be obtained when a methyl complex of mercury is treated with acetic acid:

$$(Ph_3P)_2CuCH_3 + CH_3COOH \rightarrow CH_3COOCu\,(PPh_3)_2 + CH_4\ .$$

The similarity of the infrared spectrum of the copper carboxylate complex with the spectrum of sodium acetate is evidence, according to the authors[110], for the ionic nature of the bond in the complex. The following assignment of the bands in the spectrum of the copper carboxylate complex $(Ph_3P)_2Cu(OOCCH_3)CO_2$ has been made (in terms of wavenumbers, cm^{-1}): ν(C–H) (asymm.) = 2980 (w.); ν(C–H)(symm.) = 2920 (w.); ν(OCO) (asymm.) = 1640 (s.); ν(OCO) (symm.) = 1393 (s.); $\nu(CH_3)$(rocking) = 1020 (w.); ν(C–C) = 925 (w.); ν(OCO) (symm.def.) = 622 (w.); bands corresponding to coordinated carbon dioxide: 2620 (w.); 1600 (v.s.); 1302 (v.s.); 821 (m.); 648 (w.).

When the unstable complex $[(PPh_3)_2Co(CO)C_2H_5]$, formed when acrolein interacts with the complex $(Ph_3P)_3Co(N_2)H$, was treated with CO_2, the product[103,231] was the carboxylate complex $(PPh_3)_2Co(OOCC_2H_5)_2$, which readily loses triphenylphosphine when an attempt is made to recrystallise it and is converted into cobalt propionate $Co(OOCC_2H_5)_2 . 3H_2O$.

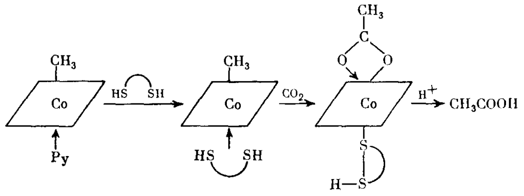
Carbon dioxide is readily inserted also in a rhodium–carbon σ bond in low-valence rhodium complexes of the type $(Ph_3P)_3RhR$, where R = CH_3 or C_6H_5, which results in the formation of carboxylate complexes of the type $(Ph_3P)_3RhOOCPh$.[232,233] When these complexes are treated with inorganic acids, the products are acids, whereas on treatment with BF_3-containing methanol the methyl esters of the corresponding acids are formed. Similar complexes may be obtained also when the complexes $(Ph_3P)_3 . RhOR$ or $(Ph_3P)_3RhOH$ are treated with stoichiometric amounts of acid in the presence of an excess of triphenylphosphine. The infrared spectrum of the benzoate complex contains bands characteristic of transition metal carboxylate complexes: ν(OCO) (asymm.) = 1608 (s.) and 1570 (s.) cm^{-1} as well as ν(OCO) (symm.) = 1360 (v.s.) cm^{-1}. According to X-ray diffraction data[231,233], the rhodium atom in the benzoate complex (Fig. 7) is coordinated to three Ph_3P ligands and the benzoate ligand via a monodentate linkage, which is very rarely encountered in transition metal carboxylate complexes. The coordination of rhodium is close to the square planar form slightly distorted owing to steric interactions between the bulky triphenylphosphine ligands.

On the other hand, many compounds containing stable transition metal–carbon σ bonds do not interact with CO_2. Thus benzylchromium $PhCH_2Cr$ is stable in a CO_2 atmosphere[234]: the attempts[62] to insert carbon dioxide in a cobalt–carbon σ bond in compounds of the type $RCo(CN)_5^{3-}$, where R = $PhCH_2$, Me, etc., were unsuccessful. However, the introduction of certain ligands into the reaction mixture favours such insertion in many instances. Thus it has been found[148] that organic nitrogen-containing bases catalyse the insertion of CO_2 in a zinc–carbon bond. The increase of the reactivity of diethylzinc in the complexes with *NNNN'*-tetramethylenediamine, bipyridyl, and *N*-methylimidazole has been explained[148] by the increased nucleophilicity of the ethyl–zinc bond:

$$Et{-}Zn{-}Et \cdot L + CO_2 \rightarrow EtCOOZnEt \cdot L\ ,$$

where L is an organic nitrogen-containing base.

It has been shown[235] that in the case of methylcobaloxime, in which the cobalt–carbon bond is exceptionally stable, the presence of thiols, which promote the polarisation of the transition metal–carbon bond, makes possible the insertion of CO_2 in a cobalt–carbon bond with formation of the carboxylate fragment:



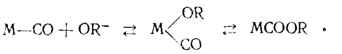
Thus the interaction of CO_2 with complexes containing a transition metal–carbon σ bond is evidently one of the pathways to the formation of transition metal carboxylate complexes. The space available in the present review precludes a detailed consideration of the properties of these compounds and we shall therefore confine ourselves merely to literature references to the employment of carboxylates in catalysis[236–248] and the preparation of the carboxylate complexes of copper[249,250], vanadium[251–254], tungsten, molybdenum[255,256], rhenium[257], iron[256,258], cobalt[259], and uranium[260], as well as a wide variety of platinum group metal complexes[261–290].

As stated at the beginning of this section, CO_2 can be apparently inserted in a transition metal–carbon bond not only with formation of carboxylate complexes but also "anomalously" with formation of metal-carboxylic acid esters, i.e. compounds containing the M–COOR fragment. Presumably factors such as a low positive charge on the metal combined with the electron-donating nature of the ligands promote this type of anomalous insertion of carbon dioxide.

Indeed the interaction of cobalt complexes containing the ethyl–cobalt σ bond with CO_2 leads to the formation of the ethyl ester of the metal–carboxylic acid as well as the cobalt carboxylate complex (see above)[103,231]. The properties of the complex $(Ph_3P)Co(CO_3)_nCOOEt$ (n = 0.5–1.0) obtained under these conditions are analogous to the properties of the familiar transition metal complexes containing the M–COOR group.

On treatment with hydrochloric acid, carbon dioxide is evolved with formation of the complex L_2CoCl_2 and ethyl formate. When the complex is treated with methyl iodide, ethyl acetate is formed in high yield, while esterification of the compound with $MeOH–BF_3$, for example, gives rise to a mixture of methyl and ethyl formates and acetates[231]. Analogous results were obtained when the known platinum, cobalt, iridium, and rhodium complexes containing the M–COOR fragment are treated with an esterifying agent of the type $ROH-BF_3$ ($R = CH_3$ or C_2H_5). On the other hand, the interaction of carboxylate complexes of the type MOOCR with the $R'OH-BF_3$ mixture leads to the formation of RCOOR′ esters only, while complexes containing the M–COOR group yield a mixture of HCOOR and R′COOR.[65]

The cobalt complex containing the Co–COOEt group, obtained in solution when the complex $(Ph_3P)_3Co(N_2)H$ is treated with methyl chlorocarbonate, is readily decarbonylated with formation of a cobalt complex containing the CO and OEt ligands. This is the reverse of the reaction involving the formation of complexes containing the M–COOR fragment when metal carbonyls are treated with alcohols:



$$M{-}CO + OR^- \rightleftarrows M\langle{}^{OR}_{CO} \rightleftarrows MCOOR\ .$$

A fairly large number of transition metal complexes which are esters of metal–carboxylic acids are already known (see, for example, Angelici's review[291]).

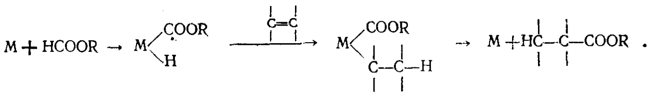
Reactions involving the rupture of a carbon–hydrogen bond in formic derivatives can be of interest for the addition of formamides or formate esters to unsaturated compounds:

$$HCOOR + {>}C{=}C{<} \xrightarrow{M} HC{-}C{-}COOR\ .$$

Table 9. The addition of ethyl formate in the presence of transition metal complexes (8 h, HCOOEt : olefin = 1 : 1).

Catalyst	Temp., °C	Initial olefin	Reaction product	Yield, moles per mole of catalyst
$(Ph_3P)_3RhCl$	140	Cyclohexene	Ethyl cyclohexanecarboxylate	5.3
$(Ph_2PH)_3RhCl$	180	ditto	Ditto	6.0
$(Ph_3P)_2Rh(CO)Cl$	180	»	»	0.8
$(Ph_3P)_2Ir(CO)Cl$	180	»	»	1.2
$(Ph_3P)Rh(CO)_2Cl$	180	»	»	3.3
$(Ph_3P)_3IrH_3$	180	»	»	0.2
$(Ph_3P)_3Os(CO)(H)Cl$	180	»	»	0.6
$(Ph_3P)_2Rh(CO)Cl$	180	$H_2C{=}CH_2$	CH_3CH_2COOEt	0
$(Ph_3P)_2Rh(CO)Cl$	180	$CH_3CH{=}CH_2$	$CH_3CH_2CH_2COOEt$	3.0
$(Ph_3P)_2Rh(CO)Cl$	180	$(CH_3)_2C{=}CH_2$	$(CH_3)_2CHCH_2COOEt$	0
$(Ph_3P)_2Rh(CO)Cl$	180	Hex-1-ene	Ethyl oenanthate	7.0

Such a reaction has been achieved[61] in the presence of various transition metal complexes (Table 9). The yield of the reaction product depends on the nature of the olefin, temperature, reaction time, and the olefin : formate ester ratio. In certain cases the dimerisation of olefins was observed as a side reaction. Rhodium compounds proved to be the most active, while platinum complexes were found to be inactive, probably mainly due to the high stability of the platinum–carbon bond. Presumably the addition of formate esters to olefins proceeds via a stage involving the rupture of a C–H bond in the esters and the formation of esters of metal–carboxylic acids as intermediates:



$$M + HCOOR \rightarrow M\langle{}^{COOR}_{H} \xrightarrow{C=C} M\langle{}^{COOR}_{C-C-H} \rightarrow M + HC{-}C{-}COOR\ .$$

It is noteworthy that the reaction of cyclohexene with the complex $(Ph_3P)Rh(CO)_2Cl_2COOEt$ led to the formation of ethyl cyclohexenecarboxylate.

In the synthesis of vinyl ethers from acetylene, alcohols, and carbon monoxide in the presence of palladium salts[292,293] the Pd–COOR fragment is formed in solution when the Pd–OR bond is acted upon by CO with subsequent transfer of the COOR group to acetylene.

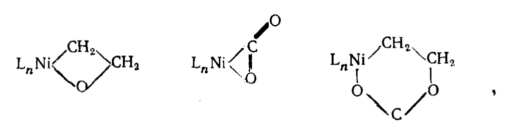
It is evident from the foregoing how large is the set of reactions associated with the problem of the insertion of carbon dioxide in a transition metal–carbon bond known at the present time. For example, the insertion of CS_2,[65, 66,294,295] or SO_2[296] in a metal–carbon bond, which is extremely common in the chemistry of organic derivatives of transition metals, may be included among reactions of this type.

VII. CATALYTIC PROCESSES WITH PARTICIPATION OF CARBON DIOXIDE

The catalytic reactions with participation of CO_2 can be divided into two main groups. The first group includes processes in which CO_2 is the starting material for the synthesis of various organic compounds, while the second group includes reactions in which CO_2 behaves as a ligand which modifies the catalyst. Processes involving the synthesis of formic acid derivatives (esters and amides) when CO_2 is reduced by molecular hydrogen to formate esters and formamides, which were discussed in Section IV, may be assigned to the first group of reactions.

Particular consideration should be given to reactions involving the reduction of CO_2 by molecular hydrogen in the presence of the graphite–$PdCl_2$–sodium heterogeneous catalyst[297]. Together with C_1–C_4 hydrocarbons, dimethyl ether is formed in high yield under mild conditions. The yield of the ether increases greatly in the presence of methanol or formamaldehyde and also when the catalyst is subjected to preliminary treatment with carbon monoxide. The formation of dimethyl ether has also been observed in the hydrogenolysis of methyl formate, which may be formed, according to the authors[297], as an intermediate in the reduction of CO_2.

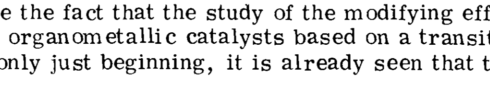
A number of workers[298-302] showed that certain organometallic compounds may catalyse the formation of polycarbonates from CO_2 and high-molecular-weight epoxides via the mechanism



$$n\left(\begin{array}{c} R \\ | \\ HC{-}CH \\ \diagdown O \diagup \end{array}\right) + n\,CO_2 \xrightarrow{Et_2Zn/water} \left(\begin{array}{c} R \\ | \\ CH_2{-}CH{-}O{-}\underset{\underset{O}{\parallel}}{C}{-}O \end{array}\right)_n - \ldots$$

Optically active polymers have been obtained by this procedure[349].

It has been shown recently[303] that the carboxylation of epoxides is catalysed by zerovalent nickel complexes. The author[303] points out the possible existence in the system of compounds of the following type:

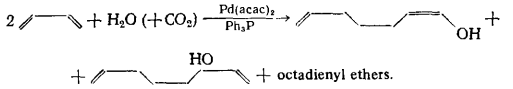


Despite the fact that the study of the modifying effect of CO_2 on organometallic catalysts based on a transition metal is only just beginning, it is already seen that this field is fairly promising from the standpoint of the synthesis of selective and specific catalysts. In this connection one should note that the use of CO_2 as the cocatalyst for the modification of the catalytic system is fairly common in the chemistry of organometallic compounds based on transition metals[62].

The influence of CO_2 on the catalytic properties of nickel, platinum, and palladium catalysts in the dimerisation of butadiene has been reported[304]. Whereas in the absence of a catalyst butadiene dimerises slowly to 4-vinyl-1-cyclohexene and CO_2 has no effect on this process, in the presence of the phosphine complex of platinum $(Ph_3P)_4Pt$ in an atmosphere of argon the yield of 4-vinyl-1-cyclohexene increases to 90–97%; a small amount of octa-1,3,7-triene is formed as a side product. When argon is replaced by CO_2, only *trans*-octa-1,3,7-triene is formed in the reaction. Similar results were obtained in the presence of the complexes $(Ph_3P)_4Pd$, $(Ph_3P)_4Ni$, and $[(PhO)_3P]_4Ni$. The authors[304] do not discuss the mechanism of the action of carbon dioxide but suggest that unstable CO_2 complexes are formed during the reaction. The attempts to isolate such complexes were unsuccessful.

It may also be that the catalysts are involved in this reaction as carbonate complexes (see Section IV). At any rate, according to the results of the same workers[305], octa-1,3,7-triene is formed from butadiene in the presence of a platinum carbonate complex.

It has been observed[306] that CO_2 has a significant influence on the formation of octadienols from butadiene and water in the presence of palladium catalysts. The interaction of butadiene and water in the presence of the $Pd(acac)_2$–triphenylphosphine system (acac = acetylacetonate) in argon leads to the formation of octatriene as the main reaction product. However, in the presence of carbon dioxide octadienols are the main reaction products and the yield of octatriene is insignificant. It is noteworthy that small amounts of carbon dioxide are sufficient for the formation of octadienols:



It is seen from the present review that the chemistry of carbon dioxide in systems involving transition metals is being as it were reborn. The data for the formation of complexes of carbon dioxide with transition metal compounds and the studies on the insertion of carbon dioxide in metal–hydrogen and metal–carbon bonds, considered in this review, demonstrate the extensive scope of the applications of these reactions in various chemical processes. Particular mention should be made of the reactions in which carbon dioxide is involved in catalytic processes, on the one hand, as the starting material for the synthesis of various organic compounds and, on the other, as a ligand modifying known catalysts.

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Reactions of Transition Metals in the Atomic State

G.A.Domrachev and V.D.Zinov'ev

The formation of organometallic compounds and π complexes by the direct action of the atomic metal on organic and inorganic compounds is surveyed. The mechanism of these reactions is examined, and practicable recommendations are given for conducting them. A list of 100 references is included.

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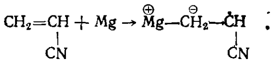
I. INTRODUCTION

During recent years research has been vigorously pursued on the reactions of various metals in the atomic state, as well as on individual valency-unsaturated species. The possibility of using atomic metals for preparative purposes has been studied[1-4]. Condensation of the vapours of magnesium and a monomer—styrene, α-methylstyrene, isoprene, acrylonitrile—together at $-196^{\circ}C$ yields yellow–orange frozen solutions. Thawing is accompanied by vigorous polymerisation, which is often explosive. Among polymerisation initiators—magnesium, zinc, cadmium, calcium, mercury—atomic magnesium has proved the most active[3,4]. Tin and lead do not exhibit activity, and in the ternary systems with a monomer and magnesium, inhibition of polymerisation has even been observed. Electron spin resonance has shown[2] that polymerisation is initiated by a radical formed by the reaction



$$CH_2{=}\underset{\displaystyle CN}{\underset{|}{CH}} + Mg \rightarrow \overset{\oplus}{Mg}{-}\overset{\ominus}{CH_2}{-}\underset{\displaystyle CN}{\underset{|}{\dot{C}H}} \quad . \qquad (1)$$

Such radicals, frozen in excess of the monomer on the cooled walls, initiate polymerisation at temperatures far below the melting point of the monomer. Extension of the fundamental reaction to the vapours of carbon[5] and transition metals[6] has now led to the establishment of a new field in the synthetic chemistry of organometallic compounds.

The Reviewers have now made a general survey of this problem, paying attention to theoretical aspects, assessing experimental methods and equipment, with the introduction of an actively and constantly extending range of compounds into reaction (1), and prospects for employing this reaction in synthetic organometallic and applied chemistry. Existing reviews[6-8] are devoted to particular problems or else give inadequate coverage of the most recent results.

Hitherto studied reactions of organic and inorganic compounds with transition metals in the atomic state can be divided into those involving addition and those involving oxidative incorporation of the metal at various bonds. The classification of organometallic compounds of transition metals according to types of ligands is at present regarded as more convenient. In reporting the factual material, however, we have slightly modified the classification by taking as basis the maximum possible number of electrons that the compound used in the synthesis is able to donate to the metal.

II. TYPES OF REACTIONS

1. Addition of Atomic Metals

(*a*) Reactions with eight-membered carbocyclic $h^8\pi$ donors (cyclo-octatetraene)

Hardly any reactions with cyclo-octatetraene have been reported, apart from a brief mention[9] of the synthesis of dicyclo-octatetraeneuranium. The cocondensation of gaseous iron with the hydrocarbon in the presence of trifluorophosphine forms $C_8H_8Fe(PF_3)_3$, the low yield of which is probably due to slight polymerisation of cyclo-octatetraene on reaction with atomic metals[10]. However, the synthesis of $(C_8H_8)_2M$ (where M = U, Th, Pu) from the dispersed metals and cyclo-octatetraene[11] indicates that these compounds can be obtained also by low-temperature cocondensation from the gaseous metals.

(*b*) Reactions with seven-membered carbocyclic $h^7\pi$ donors

Cycloheptatriene behaves differently towards different atomic metals. Thus the cocondensation of chromium vapour with cycloheptatriene gives a mixture of products, among which the complex $(C_7H_8)_2Cr$ and the component $C_{14}H_{17}Cr$ have been detected mass-spectrometrically[12-14]. The h^4-cyclohepta-1,4-diene-h^7-cycloheptatrienylchromium complex, corresponding to the compound $C_{14}H_{17}Cr$, had been described earlier[15]. The condensation of chromium vapour with cycloheptatriene and trifluorophosphine leads to the isolation of $C_7H_8Cr(PF_3)_3$,[12,14] but the cocondensation of cycloheptatriene with atomic molybdenum or tungsten gives the h^5-cycloheptadienyl-h^7-cycloheptatrienyl derivative, in which the former ligand is easily exchanged for cyclopentadienyl[16,17]. Iron vapour reacts smoothly with cycloheptatriene to give a good yield of $C_7H_9FeC_7H_7$,[13,18] in which the cycloheptadienyl and tropylium systems are coordinated to the iron atom and exhibit dynamic behaviour $C_7H_7 \rightleftharpoons C_7H_9$ in solution. The nuclear magnetic resonance and mass spectra of the product have been determined, and an X-ray structural analysis has been made[18]. Cobalt reacts with cycloheptatriene in the presence of trifluorophosphine to give an allyl derivative, h^3-cycloheptenyltetrakistrifluorophosphinecobalt, and tristrifluorophosphinecobalt hydride[19].

(*c*) Reactions with six-membered carbocyclic $h^6\pi$ donors (arenes)

The use of atomic metals has opened up wide prospects for synthesising diarene complexes of various metals, as well as complexes of functionally substituted benzene derivatives.

Diarene complexes of titanium $Aren_2Ti$ [where Aren = C_6H_6, $C_6H_5CH_3$, $C_6H_3(CH_3)_3$] have been obtained for the first time[20,21]. Dibenzenetitanium comprises reddish-orange crystals that are extremely sensitive to air; they sublime readily at 80°C (10^{-3} mmHg) and begin to decompose above this temperature. The structure of diarene complexes of titanium has been proved by the ^1H n.m.r., infrared, mass, and photoelectronic spectra[21]. In contrast to other methods, the yield of an organometallic compound obtained from the gaseous metal is a measure of the stability of the compound, since it is determined also by the reverse decomposition to the metal and the ligand. In some cases, however, the yield probably depends also on secondary processes. It is interesting to trace the variation in the yield (calculated on the metal vaporised) in a series of diarene complexes of vanadium[22-24]:

$$(C_6H_6)_2\,V\ (60\%),\ (C_6H_5CF_3)_2\,V\ (22\%),\ (C_6H_5F)_2\,V\ (13\%),$$
$$(C_6H_5Cl)_2\,V\ (7\%),\ (p\text{-}C_6H_4F_2)_2\,V\ (1\%).$$

Hexafluorobenzene forms with vanadium vapour an extremely reactive and explosive complex[22].

An immense number of diarene compounds of chromium have been obtained by the direct method. The first such derivative was dibenzenechromium[25,26], obtained in ~60% yield (calculated on the metal vaporised) by the interaction of chromium and benzene vapours. By removing the need for intermediate reagents, use of the metal in its most reactive form permits partial avoidance of the transalkylation and elimination processes that accompany Fischer reduction[27,28].

The compounds obtained include dibenzenechromium derivatives substituted by CH_3, C_2H_5, Cl, F,[12] $[CH_2]_nCOOR$ (n = 0–2),[29,30] t-C_4H_9,[19] iso-C_3H_7,[31] CF_3,[24] and C_6H_5[32] with various substituents[23,33-35]. Diarenechromium complexes have been obtained from polysubstituted arenes containing *o*-COOR,[36] *p*-F,[12] *m*-iso-C_3H_7,[31] *m*- and *p*-CF_3, and *o*-Cl.[24] Complexes have been prepared having different substituents in the ring (H, F, Cl, CH_3, CF_3) and different numbers of these substituents in the rings[33]. The ^{19}F n.m.r. spectra have been compared with those of the original organic molecules[33], and the ^{13}C n.m.r. spectra have been determined[34]. The synthesis of bisborazinechromium was reported[37], but no confirmation has subsequently appeared in the literature.

Mixed complexes can be obtained by the cocondensation of chromium vapour with a mixture of compounds:

$$Cr + Aren + n\,L \rightarrow (Aren)\,Cr\,(L)_n \qquad n = 1,\,3;\quad L = Aren',\quad PF_3\ . \tag{2}$$

Thus the complex $C_6H_6CrC_6HF_5$, stable in air, has been obtained from a mixture of benzene and pentafluorobenzene[38]. The acidic hydrogen atom in the second ligand is very readily replaced by a lithium atom on metallation with t-butyl-lithium in ethereal solution; various derivatives of the type $C_6H_5CrC_6H_5X$ could be obtained by replacing the lithium, with X = $Si(CH_3)_3$, Co_2Li, $C(CH_3)_2OH$, $CpFe(CO)_2$, $CpFeC_5H_4CHOH$.[36] Cocondensation of chromium vapour with a mixture of benzene and hexafluorobenzene gives $C_6H_6CrC_6F_6$.[32] Timms[19] obtained a series of mixed complexes $ArenCr(PF_3)_3$, where Aren = C_6H_6, C_6H_5F, 1,4-$C_6H_4F_2$, 1,3,5-$C_6H_3F_3$, 1,2,3,5-$C_5H_2F_4$, C_6HF_5, C_6F_6. The cocondensation of chromium vapour solely with hexafluorobenzene gives an extremely reactive, explosive complex[22,24].

Work on the preparation of diarene and mixed complexes of chromium, as well as vanadium complexes, reveals a tendency for the yield of the addition product to decrease with increase in the electron-accepting properties of the groups in the ring. However, certain complexes of chromium with halogenobenzenes are obtained in higher yield than are the complexes with benzene itself[12]. In a series of compounds of general formula $ArenCr(PF_3)_3$ maximum and minimum yields were obtained when the arene was respectively *p*-difluorobenzene and hexafluorobenzene[19]. An interesting distribution of yields is exhibited[24] by the compounds $[p\text{-}(CF_3)_2C_6H_4]_2Cr$ (38%), $(o\text{-}ClC_6H_4CF_3)_2Cr$ (33%), $[m\text{-}(CF_3)_2C_6H_4]_2Cr$ (17%), and $(C_6H_5CF_3)_2Cr$ (26%). The high yields of the diarene complexes of chromium containing two electron-accepting substituents in the benzene ring of the ligand are combined with unusual stability of these compounds in air. The decrease in the yields of complexes of polyhalogenated arenes is explained by an increasing tendency for dehalogenation to occur, but the high yield of $p\text{-}C_6H_4F_2Cr(PF_3)_3$ in comparison with $C_6H_6Cr(PF_3)_3$ by kinetic factors[19].

The cocondensation of chromium vapour with pyridine and trifluorophosphine produces a mixture of the two volatile compounds $\pi\text{-}C_5H_5NCr(PF_3)_3$ and $\sigma\text{-}C_5H_5NCr(PF_3)_3$[19,32]. The former is a true π complex of pyridine; it is stable in air for a short time. Its decomposition is promoted by moist air[19].

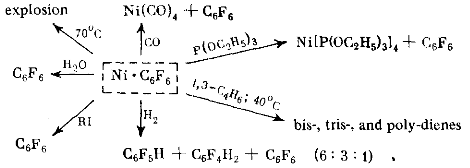
Elimination of electron-accepting groups (bromo, iodo, cyano) under the influence of the atomic metal is sometimes observed[33,37] in the preparation of diarene complexes by the cocondensation of chromium vapour with arenes. This is accompanied by resinification of the organic compound with formation of bound hydrocarbon products and chromium compounds in an oxidised state. Thus an almost theoretical yield of chromium tribromide is obtained by the cocondensation of chromium vapour with bromobenzene[33]. Analogous elimination of electron-accepting substituents from the benzene ring takes place in the Fischer preparation of diarenechromium derivatives[27,28]. The elimination is probably due to enhanced mobility of the substituent in the form of an anion in the actual diarene complex owing to transfer of electron density from the metal to the electron-accepting group.

Diarene compounds are not formed by the action of gaseous manganese on arenes[19]. The cocondensation of manganese vapour with a mixture of an arene and cyclopentadiene gives mixed complexes $ArenMnC_5H_4R$, where Aren = C_6H_6, $C_6H_5CH_3$, 1,3,5-$C_6H_3(CH_3)_3$, and R = H, CH_3.[19] Hydrogen begins to be evolved only at −120°C.[13,19] Since the reaction was conducted by feeding cyclopentadiene to the reaction vessel after the cocondensation of manganese and benzene, cyclopentadienyl derivatives are obviously not preliminary products. The yield of $C_6H_6MnC_5H_5$ calculated on the manganese vaporised is 2–3%,[13] whereas the yield of the same product from the reaction between manganese(II) chloride, phenylmagnesium bromide, and sodiocyclopentadiene is only 0.4%.[39] Direct synthesis is more convenient for the preparation of arenocene complexes of manganese, since this metal can be evaporated from a resistance vaporiser at a rate of 20–100 mg-atoms h^{-1}.[6]

The cocondensation of iron vapour with benzene obviously forms dibenzeneiron[25,31,40], but this explodes when the reaction mixture warms up to −50°C. If cyclopentadiene is added to this cocondensate at −196°C, a 40%

yield of ferrocene is formed on thawing out[25], but $C_6H_6FeC_5H_5$ is not formed. When the cocondensate of iron with benzene heats up to room temperature in an atmosphere of hydrogen, part of the benzene is hydrogenated to cyclohexane. Toluenebistrifluorophosphineiron has been isolated[40] from the cocondensation of iron vapour with toluene followed by addition of trifluorophosphine at −196°C. If buta-1,3-diene is used instead of trifluorophosphine, buta-1,3-dienetolueneiron is formed[40]. According to Timms[19] the stable eighteen-electron complex h^6-mesitylene-h^4-1,3,5-trimethylcyclohexa-1,3-dieneiron-(0) is formed by the cocondensation of iron vapour with mesitylene, but the formation of a diene ligand from this hydrocarbon is difficult to understand. With cyclohexa-1,3-diene iron vapour gives h^6-benzene-h^4-cyclohexa-1,3-dieneiron(0). When the cocondensate is heated to −20°C, the hydrocarbon undergoes catalytic disproportionation to cyclohexane and benzene.

Gaseous nickel does not react with benzene under conditions of direct synthesis. The nickel atom is not incorporated at a carbon–fluorine bond when atomic nickel acts on hexafluorobenzene[22], but an unstable, extremely reactive, and explosive complex of zerovalent nickel is formed. Proof of its formation is provided by its reactions



(3)

At low temperatures nickel probably gives unstable intermediate complexes with arenes. On heating or removal of the ligand atomic nickel undergoes aggregation to a highly active mass[24,41,42]. Like nickel, cobalt forms with hexafluorobenzene a complex that decomposes at −10°C.[22] Furthermore, mixed complexes of cobalt and nickel have been obtained, analogous to the iron compounds ArenFe.$(PF_3)_2$ and ArenFe-1,3-C_4H_6.[40]

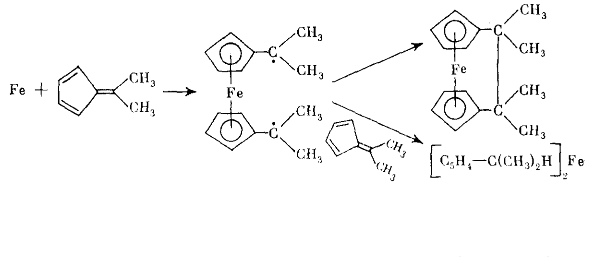
The reactions of atomic molybdenum and tungsten have been studied by two teams of investigators. Diarene complexes of molybdenum have been obtained with Aren = C_6H_6, $C_6H_5CH_3$, 1,3,5-$C_6H_3(CH_3)_3$,[20] $C_6H_5OCH_3$, $C_6H_5N(CH_3)_2$, C_6H_5F, C_6H_5Cl, and $C_6H_5COOCH_3$; and of tungsten with Aren = C_6H_6, $C_6H_5CH_3$, o-$C_6H_4(CH_3)_2$, $C_6H_5OCH_3$, C_6H_5F.[43]

Attempts to obtain arene derivatives of lanthanides (samarium, erbium) did not give definite results[9]. The volatile products obtained were not identified.

(*d*) Reactions with five-membered carbocyclic $h^5\pi$ donors (cyclopentadienyls, etc.)

These reactions are interesting if only because cyclopentadiene possesses a "spare" hydrogen atom for the formation of an h^5-C_5H_5–Metal bond. Cyclopentadiene therefore behaves differently depending on the nature of the metal.

The synthesis of ferrocene by the cocondensation of freshly distilled cyclopentadiene and iron vapour, in 60% yield based on the iron vaporised, was first reported by Timms[25]. Under these conditions nickel gave an 80% yield of h^5-cyclopentadienyl-h^3-cyclopentenylnickel. No subsequent communications have appeared on the synthesis of ferrocene, but in a review[6] Timms referred to Skell in connection with such a synthesis†. More recently the preparation of a mixture of 1,1′-di-isopropylferrocene and ferrocenophan has been reported[44] by the cocondensation of the vapours of iron and dimethylfulvene, for which the mechanism



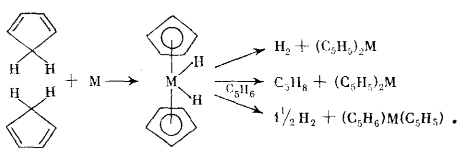
(4)

was suggested. Although the presence of bound ferrocene was not clearly demonstrated[44], the process is of great interest.

Hydrogen evolution is observed in the reaction of atomic chromium with monomeric cyclopentadiene[12], and a 50% yield of dicyclopentadienylchromium is obtained. The hydrogenation product cyclopentene is detected among the reaction products[12]. In the case of atomic cobalt the reaction with cyclopentadiene involves the formation of h^4-cyclopentadiene-h^5-cyclopentadienylcobalt in 50% yield calculated on the metal vaporised[6].

Manganese does not react with cyclopentadiene under conditions of direct synthesis (the mixed arene–cyclopentadienyl complexes have been discussed above). Especially interesting reactions occurred in the action of atomic molybdenum and tungsten on monomeric cyclopentadiene[45], when the di-h^5-cyclopentadienylmetal dihydrides were formed. The characteristics of the products agreed well with those of the compounds obtained in the traditional way[46]. The cocondensation of molybdenum or tungsten vapour with an equimolecular mixture of benzene (or an alkylbenzene) and cyclopentadiene gives a mixture of 20% of a diarene complex, 25% of a dihydride, and 55% of a monohydride[47]. The h^6-arene-h^5-cyclopentadienylmolybdenum monohydride obtained sublimes readily under 1 μmHg at 65°C. Preliminary results[47] on the action of atomic molybdenum and tungsten on indene indicate formation of a mixture of the di-indenylmetal, di-indenyl dihydride, and di-indenyl monohydride.

Thus results on the reactions of metal vapours—iron, chromium, cobalt, molybdenum, tungsten—with cyclopentadiene can be summarised on the hypothesis that all the reactions have the mechanism



(5)

A possible alternative is intramolecular dehydrogenation–hydrogenation of the h^4-cyclopentadiene ligands with their

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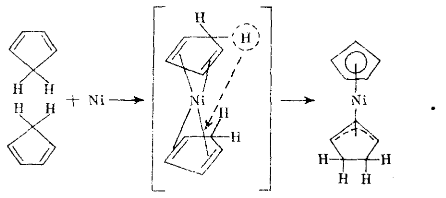
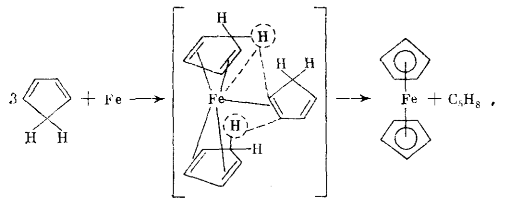
† The paper to which Timms[6] refers does not actually mention ferrocene[100].

aromatisation:



(6)

The coordinated double bond of a third cyclopentadiene molecule may also undergo intramolecular hydrogenation, facilitated by cooperation of the metal atom:



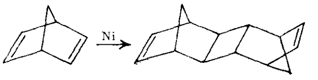
(7)

The mechanism of migration of the hydrogen atom is probably analogous to the hydride rearrangement. The stability of hydro-derivatives of transition metals (such as rhenium, niobium, tantalum, molybdenum, and tungsten) increases[48] with the atomic weight of the metal; hence, according to the above hypothesis, the same dependence should exist for the intermediate hydride complexes formed in the reaction of metal vapours with cyclopentadiene. It therefore seems to us possible that stable hydride complexes may be isolated when the vapours of other "heavy" transition metals undergo cocondensation with cyclopentadiene.

The cocondensation of nickel vapour with the *closo*-carborane $C_2B_9H_{11}$ gives the well known complex $(C_2B_9H_{11})_2Ni$.[19]

(*e*) Reactions with dialkene $h^4\pi$ donors

Reactions with cyclic dienes. The action of atomic nickel on cyclo-octa-1,5-diene gives the complex $(C_8H_{12})_2Ni^0$ [49] described earlier by Wilke[50], whereas with norbornadiene the *exo-trans-exo*-dimer is formed[49]



(8)

instead of an organometallic product. With atomic metals the former hydrocarbon gives several isostructural complexes $(C_8H_{12})_2M$, where M = Pt,[51] Fe.[10] The iron complex was synthesised at −120°C, iron being sputtered into a solution of the hydrocarbon in methylcyclohexane (other solvents have also been used). Formation of the complex is proved by its reaction with 2,2′-bipyridyl[10]:

$$(1{,}5\text{-}C_8H_{12})_2Fe + 2{,}2'\text{-Bipy} + HPF_6 \rightarrow (\text{Bipy})_2Fe(PF_6)_2 + 2\,(1{,}5\text{-}C_8H_{12})\,. \quad (9)$$

The action of trimethyl phosphite on the complex $(C_8H_{12})_2Fe$ entails[52] isomerisation of the ring with the formation of $1{,}3\text{-}C_8H_{12}Fe[P(OCH_3)_3]_3$; such isomerisation is not observed when carbon monoxide, phosphorus trifluoride, or t-butyl isocyanide is used instead of the phosphite. Bubbling nitrogen through an ethereal solution of the complex $(1{,}5\text{-}C_8H_{12})_2Fe$ and 1,2-bisdiphenylphosphinoethane gives[52] a nitrogen-containing complex $N_2FeP(C_6H_5)_2.CH_2CH_2P(C_6H_5)_2$. The complex $(1{,}5\text{-}C_8H_{12})_2Fe$ is a 16-electron compound; this governs its properties. It comprises pyrophoric crystals, which at −40°C decompose rapidly with the separation of iron. In solution in cyclo-octa-1,5-diene the complex is stable right up to 0°C. The ligands in the complex are easily replaced by cyclo-octatetraene, cycloheptatriene, and buta-1,3-diene[10].

Complexes isostructural with $(1{,}5\text{-}C_8H_{12})_2Fe$ have been obtained with cobalt, nickel, and platinum[53], among which the most stable is the cobalt complex, decomposing at −10°C. The action of atomic chromium has been studied on cyclo-octa-1,3- and -1,5-dienes[54,13]. Cocondensation of the former diene with atomic chromium in the presence of carbon monoxide involves isomerisation into the 1,5-diene, as in the reactions with molybdenum and tungsten hexacarbonyls[55]. Replacing carbon monoxide by trifluorophosphine yields[54] two compounds:

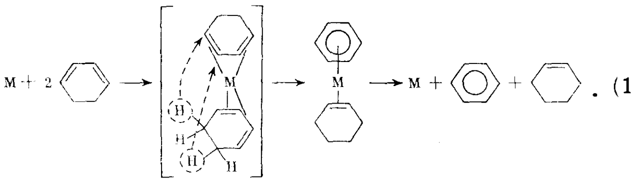
$$1{,}5\text{-}C_8H_{12} + PF_3 + Cr \rightarrow (1{,}5\text{-}C_8H_{12}Cr(PF_3)_4 + C_8H_{11}Cr(PF_3)_3H\,. \quad (10)$$

The expected cyclo-octa-1,5-dienetetrakistrifluorophosphinechromium (yield 1%) is accompanied by $C_8H_{11}Cr.(PF_3)_3H$ (yield 3%), a red solid formed also by the action of atomic chromium on cyclo-octa-1,3-diene in the presence of phosphorus trifluoride[54]. Furthermore, the complex $1{,}5\text{-}C_8H_{12}Cr(PF_3)_4$ undergoes the reaction

$$3(1{,}5\text{-}C_8H_{12})Cr(PF_3)_4 \xrightarrow{85°\,C} Cr(PF_3)_6 + 2C_8H_{11}Cr(PF_3)_3H + 1{,}5\text{-}C_8H_{12}) \quad (11)$$

when heated[54]. X-Ray examination shows[54] that $C_8H_{11}Cr.(PF_3)_3H$ is h^4-cyclo-octadienylhydrotristrifluorophosphinechromium, with the hydride hydrogen not localised on the chromium. The signal at τ = 22.4 ppm in the ^1H n.m.r. spectrum (in deuterotoluene at −50°C) is regarded as evidence of the presence of hydride hydrogen. A π-allyl hydride mechanism is postulated[54] for migration of the hydrogen atom to the ring.

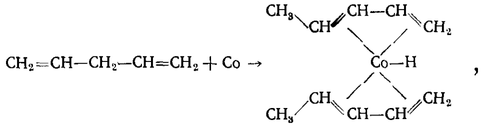
An interesting reaction is the catalytic disproportionation of cyclic dienes on cocondensation with chromium, iron, cobalt, and nickel in the vapour state. It is assumed that an intermediate complex is formed[16]:



(12)

Reactions with acyclic dienes. Products of the action of atomic metals on acyclic dienes are not always clearly defined, but there is evidence that organometallic compounds are formed. Skell and his coworkers have undertaken a series of investigations[12,16,49,56] on the reactions between atomic metals and unsaturated hydrocarbons. Whereas with atomic aluminium the main reaction is addition at the double bond (σ bond),[56] atomic nickel forms π complexes having a pure π bond[49]. Deuterolysis of the reaction products from transition metals with dienes gives the original acyclic dienes. A certain quantity of deuterium detected in them is attributed to π-allyl hydride rearrangement. The cocondensation of atomic nickel with buta-1,3-diene leaves a grey residue, probably containing bridging butadiene ligands[49], from which a volatile yellow liquid was isolated (yield 2%) that proved to be bisbuta-1,3-dienenickel(0). Dissolution of this complex in liquid butadiene at −20°C gives a dark red organonickel compound $C_{12}H_{18}Ni$, identical with the dodeca-2,6,10-triene-*centro*-nickel(0) obtained by Wilke[50], hydrogenation of which forms n-dodecane.

Gaseous cobalt is a highly active catalyst for the isomerisation of alk-1-enes into non-terminal alkenes and of non-conjugated into conjugated compounds[16]. Such catalytic reactions, as well as certain polymerisation processes, are terminated by the formation of stable complexes of cobalt and certain other metals. Thus relatively stable complexes of cobalt are formed by the reactions[16]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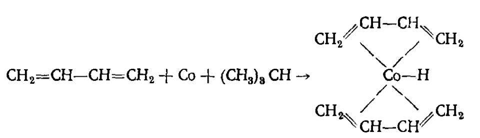
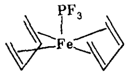

(14)

Formation of a hydride complex by the latter reaction takes place in the presence of compounds that readily liberate hydrogen.

The cocondensation of platinum vapour with buta-1,3-diene[51] gives a product that catalyses hydrogenation of excess of the butadiene at −78°C. Atomic iron on cocondensation with buta-1,3-diene yields a dark substance probably containing bridging butadiene ligands[40]. When the cocondensate was warmed up to −78°C and trifluorophosphine or carbon monoxide added, complexes $(1,3\text{-}C_4H_6)_2FeL$ were obtained, in which L = PF_3, CO, or $P(OCH_3)_3$. It is suggested[57] that the trifluorophosphine group is present in an axial position in the $(1,3\text{-}C_4H_6)_2.FePF_3$ molecule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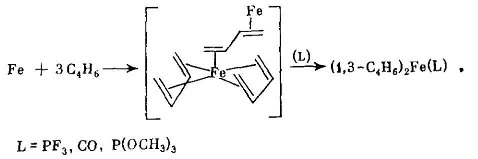
The complex of chromium with buta-1,3-diene is obtained[57] by a reaction analogous to formation of the iron complex $(1,3\text{-}C_4H_6)_2Fe$. Crystals of the complex $1,3\text{-}C_4H_6Cr(CO)_4$ decompose above 0°C.[57] Such complexes are assumed to be formed by the reaction


(15)

L = PF_3, CO, $P(OCH_3)_3$

The use of trimethyl phosphite in reaction (15) gives not only the compound $1,3\text{-}C_4H_6FeP(OCH_3)_3$ but also another complex $1,3\text{-}C_4H_6Fe[P(OCH_3)_3]_3$. In an attempt to obtain $[2,3\text{-}(CH_3)_2C_4H_4]_3Fe$ it proved impossible to isolate only $2,3\text{-}(CH_3)_2C_4H_4Fe[P(OCH_3)_3]_3$.[58]

The cocondensation of molybdenum and tungsten vapours with buta-1,3-diene gave the previously unknown trisbuta-1,3-diene complexes[59], which sublimed readily and were stable in air. X-Ray examination showed[16] that the molybdenum or tungsten atom was equidistant from all the carbon atoms.

(*f*) Reactions with three-electron *n* and *π* donors

Reactions with inorganic compounds. When chromium vapour undergoes cocondensation with nitric oxide[6] the metal is oxidised to non-volatile compounds. Several compounds containing mixed ligands, including nitrosyl, have been obtained. Thus the yield of $PF_3Mn.(NO)_3$ is 25%, although this compound is not formed by the usual synthesis under pressure; in an atmosphere of carbon monoxide (1 atm at 20°C) it is converted quantitatively into $COMn(NO)_3$. Mixed ligands have been obtained[31] with cobalt and iron, e.g. $NOCo(PF_3)_2$. Thus an attempt to obtain the already known $Co(NO)_3$ by the cocondensation of cobalt vapour and nitric oxide gave a compound that was insoluble in inorganic solvents[31], whereas $Co(NO)_3$ is readily soluble. No final conclusion was reached on the structure of the product.

Reactions with organic compounds. Timms has shown[19] that, with tetra-allyltin used as source of allyl radicals, a 20−30% yield of di-*h*³-allylnickel can be obtained by cocondensation with the atomic metal. Tri-*h*³-allyliron could not be isolated under similar conditions. When the reaction was conducted in the presence of phosphorus trifluoride, however, a paramagnetic compound $h^3\text{-}C_3H_5Fe(PF_3)_3$ separated that contained a seventeen-electron shell and was stable in air[19]. Di-*h*³-allylbistrifluorophosphineiron, which contains an eighteen-electron shell, is obtained only in insignificant quantities.

Atomic cobalt acts on propene in the presence of phosphorus trifluoride to form a mixture[19] of $h^3\text{-}C_3H_5Co(PF_3)_3$ and $HCo(PF_3)_4$.

(*g*) Reactions with two-electron *n* and *π* donors

Reactions with inorganic compounds. Reactions with phosphorus trifluoride and with carbon monoxide have been most widely studied. It is difficult to obtain carbonyl derivatives by cocondensation with metal vapours because solid carbon monoxide has a high vapour pressure at −196°C. They are therefore obtained at lower temperatures (down to that of liquid helium) or by exchange reactions at relatively high temperatures, in which carbon monoxide interacts with intermediate compounds, acting as a stabilising ligand. The compounds $Ni(PF_3)_4$, $Pd(PF_3)_4$, $Cr(PF_3)_6$, and $[Co(PF_3)_4]_2$ have been obtained in yields respectively of 100%, 70%, 65%, and 50%.[6,8,25,29] The cocondensation of iron vapour with phosphorus trifluoride gives a mixture of 25% of $Fe(PF_3)_5$ and 25% of the dinuclear complex $(PF_3)_3Fe(PF_2)_2Fe(PF_3)_3$; the unstable compound $[Co(PF_3)_4]_2$ could not be definitely characterised. The previously known compound $(PF_3)_3.Co(PF_2)_2Co(PF_3)_3$[60] is not formed in this reaction. Like cobalt, iron forms a dinuclear complex[59] containing difluorophosphino-bridges.

The complexes $Ni(PF_2Cl)_4$ and $M[P(CH_3)_3]_4$ have been obtained with chlorodifluorophosphine and with trimethylphosphine, where M = Ni, Co, Pd.[59] The cocondensation of iron vapour with trimethylphosphine gave the previously unknown complex $Fe[P(CH_3)_3]_5$,[59] an extremely reactive solid. This compound is assumed to result from secondary reactions occurring on heating. The cocondensate of iron vapour and trimethylphosphine at −196°C is green, whereas the compound isolated is yellowish red. Nickel will form several complexes with phosphine[6,59]. The cocondensation of nickel vapour with phosphine at −196°C is accompanied by hydrogen evolution, which intensifies when the cocondensate heats up to room temperature. Tetraphosphinenickel could not be isolated because of the instability of the complex: only the mixed complex $Ni(PF_3)_2(PH_3)_2$ is obtained; it decomposes slowly above 0°C, but in the presence of phosphorus trifluoride is quantitatively converted into $Ni(PF_3)_4$.[59]

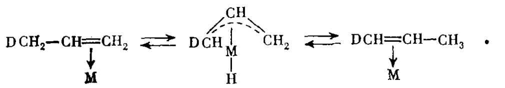
An interesting reaction, unique of its kind, occurs between nickel vapour and carbon dioxide:

$$Ni + CO_2 \rightarrow NiO + CO + Ni(CO)_4 \ . \qquad (16)$$

The tetracarbonyl is formed in 10% yield[8]. The formation of $Ni(CS)_4$ as an analogue of the tetracarbonyl is confirmed by infrared spectroscopy and mass spectrometry[61].

Many papers have appeared recently on the use of vibrational spectroscopy to study the action of atomic metals on various substances. Cocondensation of the metal with the substance has been conducted in an argon matrix at the temperature of liquid helium. This has proved the formation of carbonyls of various metals—nickel, chromium, manganese, iron, cobalt, europium, holmium, praseodymium, rhodium, neodymium, palladium, platinum, copper, silver, and iridium[13,62–71]—as well as carbonyls of intermediate composition. The formation of aluminium carbonyls $Al_x(CO)_2$ indicates[72] that carbonyl derivatives can be obtained with most metals. Complexes of nickel and palladium with molecular nitrogen $Ni(N_2)_n$ and $Pd(N_2)_m$, where $n = 1-4$ and $m = 1, 3$, are formed[73–75] at the temperature of liquid helium.

Reactions with alkenes. Skell and his coworkers[12,49,51,56] have shown how the character of the metal–alkene bond changes on passing from aluminium to chromium and then to nickel and cobalt. Deuterolysis of the organometallic products and analysis of the substances isolated has enabled the character of this bond to be deduced. True π complexes are assumed to be formed with nickel, and a certain proportion of σ bonding is postulated in the case of complexes of chromium with alkenes. It is often impossible to isolate individual compounds from the cocondensation of transition-metal vapours with alkenes, but the latter undergo various processes of catalytic conversion. Nickel and cobalt are the most active. The cocondensation of nickel and but-1-ene is accompanied by catalytic isomerisation into but-2-ene.[49] Similar isomerisation is observed[12] in the cocondensation of but-1-ene with chromium. The cocondensation of platinum with propene gives a grey substance, in which they are assumed[51] to be present in the proportions 1 : 1. π-Allyl hydride rearrangement as a mechanism of isomerisation of alkenes is confirmed by the selective cocondensation of nickel with 2- and 3-deuteropropenes[16]:



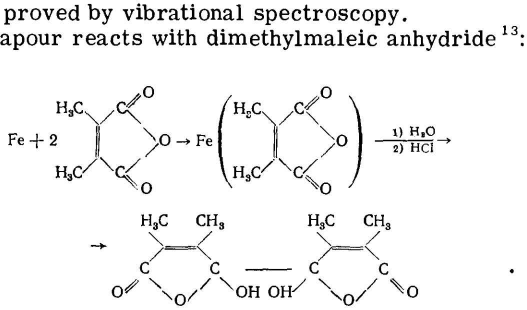
$$DCH_2{-}CH{=}CH_2(\downarrow M) \rightleftarrows DCH{\cdots}CH{\cdots}CH_2(M{-}H) \rightleftarrows DCH{=}CH{-}CH_3(\downarrow M) \ . \qquad (17)$$

This mechanism makes it clear why the quantity of 2-deuteropropene in the initial mixture remains unchanged, and why 1-deuteropropene appears after the reaction.

Attempts to prepare alkene–metal complexes isostructural with the known compound $(C_2H_4)_3Ni$ succeeded in yielding $(C_2H_4)_3Co$ and $(C_2H_4)_3Pd$ (decomposing at −60 and −30°C respectively)[53,76]. Alkene complexes of iron and chromium have not been detected. Bicyclo[2,2,1]heptane gave coloured complexes of palladium, chromium, and cobalt; the palladium complex $(C_7H_{10})_3Pd$ breaks down only at +5°C.[76]

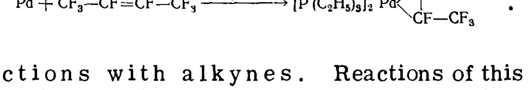
The formation of π complexes by the cocondensation of silver and copper vapours with ethylene or perdeuteroethylene has been confirmed by electron spin resonance[77]. Gold atoms did not form complexes with ethylene. The formation of copper complexees $(C_2H_4)_nCu$, with $n = 1-3$, has been proved by vibrational spectroscopy.

Iron vapour reacts with dimethylmaleic anhydride[13]:



(18)

The pyrophoric product (yield 10–15%) does not react with carbon monoxide. Hydrolysis of this compound of unknown structure leads to the linking of two anhydride molecules. The cocondensation of palladium vapour with perfluorobut-2-ene in the presence of triethylphosphine involves an interesting reaction[24]:



$$Pd + CF_3{-}CF{=}CF{-}CF_3 \xrightarrow{P(C_2H_5)_3} [P(C_2H_5)_3]_2Pd\Big\langle\begin{matrix} CF{-}CF_3 \\ | \\ CF{-}CF_3 \end{matrix} \ . \qquad (19)$$

Reactions with alkynes. Reactions of this type have been little studied. The cocondensation of nickel with alkynes gives mixtures of 1,2,4- and 1,3,5-trialkylbenzenes[49]. Trimerisation of alkynes is observed[12] also under the influence of atomic chromium. But-2-yne forms hexamethylbenzene, but terminal alkynes (but-1-yne, pent-1-yne) give mixtures of isomeric 1,2,4- and 1,3,5-trialkylbenzenes[12]. The low yield of these products does not indicate catalytic conversion, but analysis of the reaction products shows the presence of diarene complexes. Such complexes could have been postulated as intermediate compounds, promoting trimerisation of the alkynes. Obviously, only one arene ring is formed, which is attached for a certain time interval to the chromium.

Styrene undergoes polymerisation on cocondensation with iron vapour[58]. If the cocondensate heats up in an atmosphere of carbon monoxide to −20°C, a mixture of derivatives $C_6H_5CH : CH_2Fe(CO)_n$ is formed in which $n = 3-5$. Hardly any trimerisation of styrene takes place: the yield of triphenyl is ~1%.[58]

Molecular spectroscopy has been used[79] to investigate the action of nickel, palladium, and platinum on alkynes (hex-1-yne, 3-chloropropyne), but no concrete conclusions were reached on the formation of a definite type of complexes.

2. Incorporation of Atomic Metals

(*a*) Incorporation of atomic metals at carbon–halogen bonds

On cocondensation with an allyl halide atomic nickel gives the π-allylnickel halide[80]. The yield of the bromide is 80%, and that of the chloride 75%, but the product is contaminated with a mixture of C_{10-15} hydrocarbons. The cocondensation of platinum vapour with allyl chloride gives a yellow solid that decomposes at 160–170°C; reaction with triphenylphosphine forms $[C_3H_5PtCl.(C_6H_5)_3P]_x$, a compound known previously. The action of platinum on allyl chloride is assumed[51] to give a polymeric compound $(C_3H_5PtCl)_x$. The most widely reported reactions with nickel and palladium involve oxidative incorporation of the metal at the bond between an aryl, alkyl, or acyl carbon atom and the halogen:

$$M + RHal \rightarrow RMHal$$
$$M{=}Ni,\ Pd;\quad Hal{=}Cl,\ Br,\ I;\quad R{=}C_6F_5,\ C_6H_5,\ CF_3,\ CH_3,\ C_3F_7,\ C_3H_7. \tag{20}$$

The stability of the products is largely determined by the radical R.[81,82] Pentafluorophenylpalladium bromide (yield 13%) was a stable, greasy, orange-brown compound, which separated at room temperature and atmospheric pressure. It is stable in air for a short time. Its properties confirm its structure:

$$C_6F_5PdBr + Cl_2 \rightarrow C_6F_5Cl + PdClBr\ , \tag{21}$$

$$C_6F_5PdBr \xrightarrow[\text{(in benzene)}]{\Delta} C_6F_5{-}C_6F_5 + PdBr_2 + Pd\ . \tag{22}$$

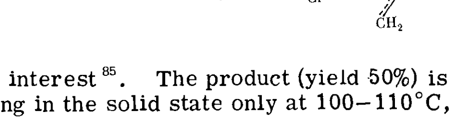
The freshly prepared bromide is able to react instantaneously with triphenylphosphine at room temperature, forming pentafluorophenylbistriphenylphosphinepalladium bromide as a white solid[81]. Pentafluorophenylpalladium bromide exists as a polymer in the solid state and as a dimer in solution. It reacts readily with various phosphine derivatives even at low temperatures. The PR_3 groups are assumed[83] to enter the *trans* position. Since compounds of type RMX are for the most part unstable, they have been isolated as complexes with phosphines[81-84]. Nickel and palladium exhibit great similarity of behaviour in reactions of incorporation, but the resulting nickel compounds are always less stable than the corresponding palladium compounds. Study of a large number of compounds has shown that incorporation of atomic palladium at a carbon–halogen bond becomes less easy according to the nature of the halogen in the sequence I > Br > Cl. The stability of the RPdHal compounds depends on the nature of R and diminishes in the sequence[24,84]

$$C_6F_5 > CF_3 \approx C_2F_5 \approx n\text{-}C_3F_7 > C_6H_5 > CH_3 \approx C_2H_5 \approx CF_2Br \approx iso\text{-}C_3F_7\ ^{24,\,84}.$$

All arylpalladium halides decompose thermally to the biaryl, palladium, and the palladium dihalide.

Metals can be incorporated at carbon–halogen bonds also in acyl halides[84]. The products RCOMHal decompose readily with decarbonylation[24,84]. The stability of the compounds RCOMHal diminishes according to the nature of R in the sequence $n\text{-}C_3F_7 > CF_3 > C_6F_5 > C_6H_5 > CH_3 > C_3H_7$.[84]

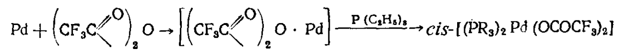
The incorporation of palladium into benzyl chloride



(23)

is of great interest[85]. The product (yield 50%) is stable, decomposing in the solid state only at 100–110°C, but in solution at 40°C. Such surprising stability, and also the spectral characteristics, indicate the presence of a π-allyl type of bond. There are data suggesting strong distortion of the benzene structure.

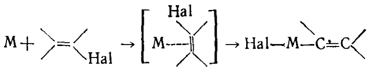
The cocondensation of palladium with trifluoroacetic anhydride followed by the addition of triethylphosphine involves the unusual reaction



$$Pd + \left(CF_3C\overset{O}{\diagup}\right)_2O \rightarrow \left[\left(CF_3C\overset{O}{\diagup}\right)_2O\cdot Pd\right] \xrightarrow{P(C_2H_5)_3} cis\text{-}[(PR_3)_2Pd(OCOCF_3)_2] \tag{24}$$

which is not finally understood[83]. The product is the salt-like bistriethylphosphinepalladium bistrifluoroacetate. A complex of a molecule of trifluoroacetic anhydride with a palladium atom is assumed to be formed as intermediate, but its structure is not yet clear.

The literature contains a brief mention[24] of reactions of platinum and titanium vapours yielding compounds of type RMX. Platinum gives the quite stable pentafluorophenylplatinum bromide, which reacts with triphenylphosphine. The *cis*- and *trans*-adducts are thus obtained, whereas the nickel and palladium analogues give only the *trans*-complexes. The compound "C_6F_5TiBr" is extremely unstable, and such a structure has only been postulated[24]. The cocondensate of titanium with bromopentafluorobenzene is able to cause the vigorous, almost explosive polymerisation of buta-1,3-diene at −78°C. The compound "C_6H_5TiBr" could not be stabilised by reaction with triphenylphosphine. An unsuccessful attempt was made[24] to incorporate palladium atoms at the C–CN bond in benzonitrile and benzilonitrile. Stereochemical aspects of incorporation in optically active compounds (1,1,1-trifluoro-, 2-chloro-, and 2-phenyl-ethanol) have been studied, and the results may be expected shortly[24]. The character of the bond (π or σ) in complexes of nickel, palladium, and platinum with halogenated alkenes



has been investigated[24].

No examples have been reported of the incorporation of transition-metal atoms at carbon–fluorine bonds. However, the formation of complexes of metals with hexafluorobenzene[22] involves vigorous decomposition of the cocondensate, probably owing to the exothermal character of the formation of metal–fluorine bonds. Incorporation of a metal at a carbon–fluorine bond occurs in the cocondensation of calcium with hexafluorobenzene[86].

(*b*) Dehalogenation with transition-metal atoms

One of the first reactions of this type was conducted by Timms[87,88], by the cocondensation of copper vapour with boron trichloride:

$$Cu + 2BCl_3 \rightarrow 2CuCl + B_2Cl_4\ .$$

With the proportions $Cu : BCl_3 = 1 : 6$ a 40% yield of B_2Cl_4 is obtained, which increases to 70% when the proportions are 1 : 20. In the cocondensation of copper vapour with methylboron dichloride in the proportions 1 : 6 the yield of $(CH_3)_2B_2Cl_2$ is 35% calculated on the copper vaporised.

Gold on cocondensation with ethyl bromide[19,32] gives products—butane, ethane, and ethylene—of the dimerisation and disproportionation of the ethyl radical, together with gold(I) bromide. Ethyl chloride does not react with gold. The cocondensation of nickel with ethyl bromide[19] forms a mixture of hydrocarbons—ethylene, ethane, and butane—in the molecular proportions 1 : 1 : 6; the residue contains much free nickel and a small quantity of its dibromide. The yield of hydrocarbons based on the nickel vaporised is only 10%: i.e. nickel is not such an effective dehalogenating metal as copper, gold, and silver. These three atomic metals are more selective reagents than are the alkali metals[19]: the product of the reaction of the optically active s-butyl chloride with copper and silver vapours retains 70% of the activity[19], whereas sodium gives the completely inactive 3,4-dimethylhexane.

It is of practical interest to obtain adducts of nickel with solvents[24,41,42]. On cocondensation with oxolan nickel gives a stable adduct, which is a good reagent for binding alkyl halides. Thus allyl bromide or benzyl chloride can be bound by means of the nickel–oxolan adduct at 40°C.

3. Reactions of Atomic Transition Metals with Compounds containing Active Hydrogen

(*a*) Synthesis of acetylacetonates

The preparation of chromium and iron acetylacetonates by cocondensation of the metal vapours with pentane-2,4-dione in the presence of oxygen was first reported by von Gustorf[89]. The yields of $CrAcac_3$ and $FeAcac_3$ were respectively 32% and 24%. In the absence of oxygen, compounds of the type $MAcac_2$ were obtained[13,63] with manganese, nickel, copper, iron, zinc, tin, and palladium in respective yields of 30%, 36%, 10%, 25%, 28%, 11%, and 10%. The aluminium complex $AlAcac_3$ has also been obtained, as well as acetylacetonates $MAcac_3$ of the rare-earth metals—erbium, dysprosium, and holmium[63].

(*b*) Reactions with alcohols

Chromium vapour reacts with methanol to form the methoxide $Cr(OCH_3)_3$ in 28% yield[13]. Reaction goes readily with isopropyl and t-butyl alcohols, but sparing solubility results in difficulties in purifying the products.

(*c*) Reactions with acids

Chromium reacts with hydrogen chloride at −196°C with the liberation of one mole of hydrogen per gram-atom of chromium vaporised[16]. Cocondensation with acetic acid yields a mixture of bi- and ter-valent salts, the relative composition of which depends on the experimental conditions[13].

(*d*) Reactions with water

Chromium reacts with water at −196°C to liberate half a mole of hydrogen, and the other half appearing on heating[16]. Atomic molybdenum and tungsten do not react with water at −196°C.

III. MECHANISM OF THE COCONDENSATION OF ATOMIC METALS WITH ORGANIC AND INORGANIC SUBSTANCES

No published assessment is available on the mechanism of the condensation of metal vapours with various substances (vapour-phase synthesis). The Reviewers feel it possible to consider this process by applying equilibrium thermodynamics to the direct synthesis of dibenzenechromium. An earlier thermodynamic calculation showed[90] that the equilibrium constant of the decomposition of dibenzenechromium

$$(C_6H_6)_2Cr\ (g) \rightleftarrows Cr\ (s) + 2C_6H_6\ (g) \tag{25}$$

increases with rise in temperature from 298 to 1000 K. Furthermore, calculation over the ranges 298–800 K and 10^{-5}–10^{7} atm showed that only at 10^{7} atm does the Gibbs free energy of process (25) change sign, i.e. that the equilibrium shifts towards formation of the complex.

To elucidate the mechanism of direct synthesis, which may be either a gas-phase or a gas–solid reaction, we can calculate the changes in Gibbs free energy ΔG (in kcal $mole^{-1}$) for the possible reactions under these conditions (chromium was regarded in the calculations as an ideal gas):

$$Cr\ (s) + 2C_6H_6\ (g) \xrightleftharpoons{298\ K} (C_6H_6)_2Cr\ (g) \quad (\Delta G = 27.2) \tag{26}$$

$$Cr\ (s) + 2C_6H_6\ (g) \xrightleftharpoons{298\ K} (C_6H_6)_2Cr\ (s) \quad (\Delta G = 18.9) \tag{27}$$

$$Cr\ (g) + 2C_6H_6\ (g) \xrightleftharpoons{298\ K} (C_6H_6)_2Cr\ (g) \quad (\Delta G = -57.4) \tag{28}$$

$$Cr\ (g) + 2C_6H_6\ (g) \xrightleftharpoons{298\ K} (C_6H_6)_2Cr\ (s) \quad (\Delta G = -65.5) \tag{29}$$

$$Cr\ (g) + 2C_6H_6\ (l) \xrightleftharpoons{298\ K} (C_6H_6)_2Cr\ (s) \quad (\Delta G = -62) \tag{30}$$

$$Cr\ (s) + 2C_6H_6\ (s) \xrightleftharpoons{77\ K} (C_6H_6)_2Cr\ (s) \quad (\Delta G = 16.4) \tag{31}$$

$$Cr\ (g) + 2C_6H_6\ (s) \xrightleftharpoons{77\ K} (C_6H_6)_2Cr\ (s) \quad (\Delta G = -70) \tag{32}$$

$$Cr\ (g) + 2C_6H_6\ (g) \xrightleftharpoons{1000\ K} (C_6H_6)_2Cr\ (g) \quad (\Delta G = -30.3)\ . \tag{33}$$

It thus becomes clear that reactions (28)–(30), (32), and (33) must be regarded as thermodynamically probable. Experimental observations indicate that equilibria (26), (27), and (31) are displaced to the left, since on the termination of synthesis the reaction vessel contains metallic chromium as a powder formed by the aggregation of atomic chromium and unable to react with benzene under normal conditions. Furthermore, the thermodynamically permitted reactions (28), (29), and (33) require a three-body collision, whose probability z_3 is almost zero: its ratio to the probability z_2 of a bimolecular gas-phase reaction is $0.01p$, where p (atm) is the pressure at 300 K;[91] since under conditions of direct synthesis $p = 10^{-4}-10^{-6}$ mmHg (i.e. $10^{-6}-10^{-8}$ atm), it becomes obvious that the probability of a three-body collision $z_3 = (10^{-8}-10^{-10})z_2$ is extremely small. As the free path of metal atoms at such pressures exceeds considerably the dimensions of all the reaction vessels used, direct synthesis must obviously be regarded as a gas–solid (metal–benzene) reaction (32). From this several conclusions may be reached concerning the mechanism of direct synthesis.

A metal atom incident on the surface of a condensed organic or inorganic substance will obviously lose its energy at the first collision with molecules of the latter (this can be deduced from the estimated kinetic energy of the atom). The local heating of the condensed phase facilitates diffusion of the metal atom and of molecules of the latter, which promotes the three-dimensional orientation favourable for interaction in the matrix. Intense vaporisation of the metal increases the probability of mutual encounter of the metal atoms and their aggregation. With inadequate dissipation of heat and the freezing of a thick layer on the walls of the reaction vessel, moreover, the substance may melt (reaction 30). The gas–liquid reaction is permitted thermodynamically, but the probability of mutual encounter and aggregation of metal atoms will be especially high under these conditions. In the condensed state the metal no longer reacts. This may explain the diminished yield of organometallic compound (relative to the theoretical yield based on the metal vaporised) and the formation of a metal powder, although the yield is governed, of course, also by the reverse decomposition of the organometallic compound to the metal and the organic compound.

The isolation of the metal atoms in the matrix can be assessed by means of the ratio of the number M of matrix atoms or molecules to the number R of metal atoms in the matrix. The spectroscopy of atoms isolated in a matrix[92] indicates that good isolation of atomic metals is achieved with $M/R \geqslant 300$. However, such data apply to a matrix which is inert with respect to the metal. Work on direct synthesis usually employs ratios of $M/R = 6-100$, since a large excess of the substance is obviously unnecessary, because of interaction with the atomic metal.

Further cooling of the walls of the reaction vessel (to the temperature of liquid helium) confers great "rigidity" on the matrix, and thereby impedes diffusion of the metal atoms and diminishes the probability of their aggregation. Furthermore, compounds that are unstable at the temperature of liquid nitrogen can be recorded spectroscopically at the lower temperature.

The above estimate provides a better understanding of the relation of direct synthesis to the thermal decomposition of organometallic compounds, e.g. a diarenechromium, which in turn enables us to assess the stability of an organometallic compound from its yield. The phase in which the metal separates plays an important part in displacing the equilibrium in thermal decomposition. Thus when chromium atoms are adsorbed on a solid (substrate) or when they aggregate to form a solid phase of metallic chromium, the synthesis–decomposition equilibrium should shift towards breakdown of the diarenechromium, because of the low mobility of chromium atoms in the solid phase. Calculation for the gas-phase reaction (33) at 1000 K shows, however, that the equilibrium is again displaced towards synthesis of dibenzenechromium if the chromium is in the gaseous state. In direct synthesis the chromium atom incident on the layer of condensed substance is more mobile than the chromium atom in contact with the substrate in the case of thermal decomposition, and the translational motion of the atom can be regarded as terminated only on formation of the organometallic compound or as a result of mutual aggregation of the atoms.

Analogous calculations can be made for the formation of ferrocene from atomic iron and cyclopentadiene:

$$\mathrm{Fe}\ (g) + 3\mathrm{C_5H_6}\ (g) \xrightleftharpoons{298\ \mathrm{K}} (\mathrm{C_5H_5})_2\mathrm{Fe}\ (g) + \mathrm{C_5H_8}\ (g)\ \ (\Delta G = -112) \tag{7}$$

$$\mathrm{Fe}\ (g) + 2\mathrm{C_5H_6}\ (g) \xrightleftharpoons{298\ \mathrm{K}} (\mathrm{C_5H_5})_2\mathrm{Fe}\ (g) + \mathrm{H_2}\ \ (\Delta G = -97) \tag{34}$$

$$\mathrm{Fe}\ (g) + 2\mathrm{C_5H_6}\ (g) \xrightleftharpoons{298\ \mathrm{K}} (\mathrm{C_5H_5})_2\mathrm{Fe}\ (g) + 2\mathrm{H}\ \ (\Delta G = +1)\,. \tag{35}$$

The free energies of these reactions at 77 K could not be calculated, unlike the case of the synthesis of dibenzenechromium, owing to the absence of thermodynamic characteristics for solid cyclopentadiene and of data on the temperature dependence of its heat capacity. However, these calculations suggest that reactions (7) and (34) will be thermodynamically feasible, involving as transition state a hydride or an eighteen-electron complex of iron (II, 1*d*). The existence of such an intermediate eighteen-electron iron complex [Eqn. (7) in II, 1*d*] can be regarded as proved by the presence in the reaction mixture of cyclopentene in equimolecular proportions to the ferrocene isolated[93].

IV. APPARATUS FOR DIRECT SYNTHESES

1. Vacuum System and Reaction Vessel

An ordinary high-vacuum system (Fig. 1), having fore vacuum and diffusion pumps, was used for the direct syntheses‡. The rate of evacuation can be increased by supplementing these with a booster pump, but normally this is not required, since the walls of the reaction vessel, cooled to −196°C, provide effective cryogenic evacuation of the substance supplied to the reaction vessel, by freezing it and thereby maintaining a high vacuum in the system.

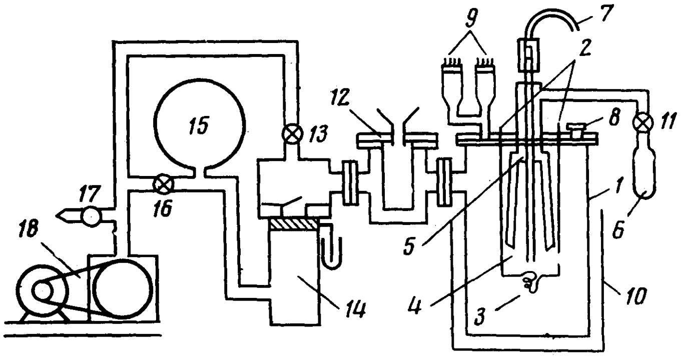


Figure 1. Diagram of apparatus for direct synthesis: 1) reaction vessel; 2) current leads; 3) vaporiser coil; 4) tube for supply of metal; 5) tube for supply of compound; 6) ampoule containing compound; 7) ampoule containing metal fragments; 8) viewing window; 9) manometric valves; 10) Dewar vessel; 11, 13, 16, 17) vacuum taps; 12) trap; 14) VA-01-1 vacuum unit; 15) ballast volume; 18) preliminary vacuum pump.

One or two traps filled with liquid nitrogen are placed between the high-vacuum system and the reaction vessel. They comprise detachable Dewar vessels. The reaction vessel with a flanged coupling and a copper or aluminium gasket is connected to the high-vacuum system through traps. Of the two forms of reaction vessel—with rigid coupling or rotating—the latter uses the same principle as in the rotary vaporiser, which is used in chemical laboratories for the vacuum evaporation of solvents. A complication in the present case is to make a stuffing box capable of rotation and operating in the pressure range $10^{-5}-10^{-6}$ mmHg (Fig. 2)§.

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‡ In our laboratory the apparatus was based on a standard VA-01-1 vacuum unit. It is convenient to use as the ballast volume the inner vessel of an ASD-15 Dewar flask. Such a metal ballast volume is safe in operation and has a large capacity (15 litres).

§ The firm G.V. Planer Ltd. (Great Britain) manufactures equipment with a rotating glass reaction vessel (diameter 100 mm) and a resistance vaporiser; an electron-beam gun of type EBSI/H is also produced by the same firm.

The overall arrangement of the apparatus is straightforward, and solving the design problem of the rigidly fixed vessel presents no great difficulty. Cooling the walls of the reaction vessel gives rise to certain difficulties, since the use of glass Dewar vessels under these conditions is complicated by the relatively large diameter of the reaction vessel. The latter should therefore have a double or triple jacket (with the outer vessels connected to the vacuum system, while the inner vessel serves for pouring the liquid nitrogen) or else the reaction vessel should be immersed in a reservoir of liquid nitrogen, for which purpose a tank cast from foam plastic can be recommended. All the various forms of apparatus differ in the ways in which they solve the problem of vaporising the metal and feeding the organic or inorganic substance to the reaction vessel.

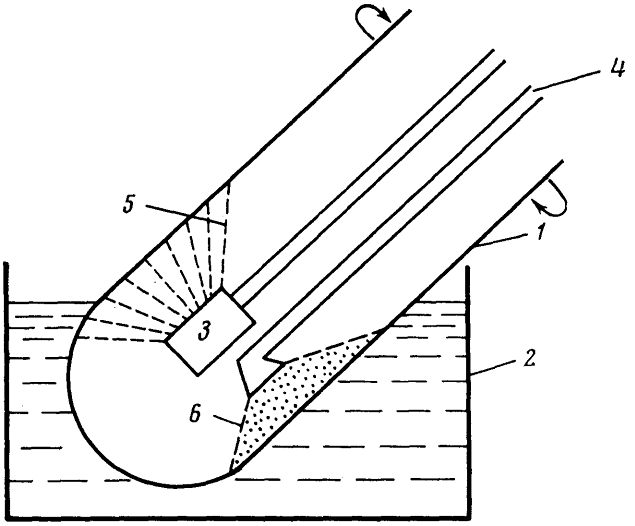

Figure 2. Diagram of rotating reaction vessel: 1) reaction vessel; 2) Dewar vessel; 3) electron gun; 4) delivery of compound; 5) metal vapour; 6) vapour of compound.

2. Vaporisation of the Metal in a Vacuum

The technology of the vacuum evaporation of metals is now well developed. Among the main methods for vaporising a metal—(*a*) from a resistance-heated vaporiser, (*b*) by induction heating of the metal in a container, (*c*) by electron bombardment of a specimen of the metal, and (*d*) by a laser beam—method (*a*) is the simplest and most practicable, but its application is restricted by the difficulty of vaprosing refractory metals. Processes (*b*) and (*c*) have the greatest prospects and are most convenient.

(*a*) Vaporisation from a resistance-heated vaporiser

In this process the metal vapour is obtained from a resistance-heated vaporiser basket made of tungsten or molybdenum wire (diameter 1–1.5 mm). The required shape is conferred on the vaporiser by means of a threaded conical mandrel (tungsten wire is wound on the cone while being heated in a flame). Such an evaporator is fixed in the clips of the current leads, which are situated in the flanged lid of the reaction vessel and are usually cooled with water.

The difficulty with a resistance evaporator is that the molten metal begins to flow along the coil and to "short" it, when vaporisation almost ceases and the coil burns out; at the same time the unmelted solid metal has a low vapour pressure and its rate of vaporisation is very small. Wetting of the coil with the molten metal can be avoided by using crucibles comprising the same vaporisers as before, but coated with aluminium or beryllium oxide[94]; such a coating is applied from an aqueous suspension of alumina¶. Use of a resistance evaporator permits the vaporisation of transition metals of the first series, copper, silver, gold, palladium, uranium, and also lanthanides. The employment of crucibles coated with aluminium oxide is restricted by the possibility of interaction with the molten metal. Such interaction takes place with chromium, and more electropositive metals cannot be vaporised from such a crucible.

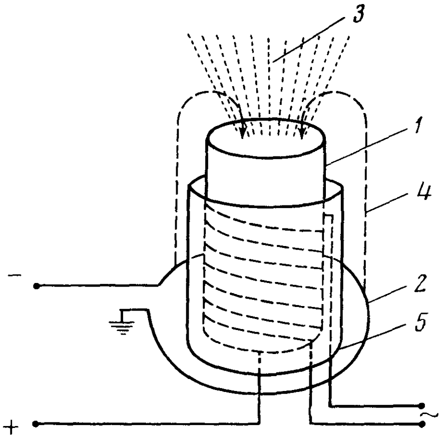

Figure 3. Diagram of electron gun: 1) crucible containing metal specimen (having a high positive potential) preheated by a coil; 2) preheated tungsten wire; 3) metal vapour; 4) flux of electrons; 5) cylindrical shield (having a slight negative potential).

Vaporisation can be effected by other modifications of this method. (i) The vaporiser may consist of a tungsten rod (diameter 3–4 mm) on which are wound in parallel a wire of the metal to be evaporated and a thin tungsten wire (diameter 0.3–0.5 mm). (ii) In the exploding wire method [57] a wire descending from a special container short-circuits the contacts and burns up, with production of a high density of metal vapour; here, however, polyatomic

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¶ The crucible coating can be applied as a paste—aluminium in a silicate cement—the coated crucibles first being dried at 200°C and then annealed in a vacuum.

metal particles are formed. (iii) The vaporiser can be made from rolled molybdenum, tungsten, or niobium–tantalum alloy (combustion boat).

The source of supply for resistance vaporisers is an adjustable transformer capable of giving currents up to 100–150 A at voltages of 6–12 V.

(*b*) Induction heating

This method has advantages over the resistance heating of a metal specimen, but is hardly used at all in apparatus for the direct synthesis of organometallic compounds. It also has its problems in connection with the need to use a high-frequency oscillator[95].

(*c*) Electron bombardment

An electron gun is used in which the electrons emitted by a tungsten filament are focussed on a specimen of the metal to be vaporised. A compact design of electron gun has been proposed by the English firm G. V. Planer Ltd. (type EBSI/H) (Fig. 3).

Choice of power for the electron gun must be based on the enthalpy of vaporisation of the metal, the desired rate of evaporation, and also the inevitable accompanying energy losses. If the power is insufficient, the metal specimen may be preheated by a different method, e.g. resistance heating.

(*d*) Laser vaporisation

Use of a laser beam to vaporise metals in direct syntheses has been reported by von Gustorf[13,57]. A carbon dioxide laser of power 1.2 kW was focussed into a spot of diameter 1–2 mm. Vaporisation of metals of high melting point was effected from a heated crucible into which the laser beam was directed.

The dependence of the reflecting power of the metal on the wavelength must be taken into account for optimum utilisation of the laser energy. The most acute problem in the use of a laser is the "window" in the reaction vessel. Thus, whereas with other methods of heating metals a "window" is necessary only for periodic observations, being closed for the remaining time and not coated with a film of the condensed metal, in the present method the "window" should be open continuously for passage of the laser beam. A "sluice" is arranged to protect the "window" from sputtering in the evacuated reaction vessel: the pressure in the "sluice" is maintained at 0.1–0.01 mmHg by a jet of argon, which blows away metal atoms (of very small volume) travelling in the direction of the "window"[13].

3. Supply of Organic or Inorganic Substance

The supply of gases to the reaction vessel is structurally very simple, being effected through orifices in a tube placed at the centre of the vessel. The supply is controlled by means of a finely adjustable tap. Volatile liquids are supplied in the same way as gases, but organic compounds of high boiling point must be heated in an ampoule, and the whole tube along which they pass to the reaction must be warmed (to prevent their condensation inside the tube). A gaseous substance is uniformly distributed in the reaction vessel, and condenses on the walls. Delivery can be simplified by uniformly spraying the substance into the reaction vessel, since a gas–solid (metal–condensate) reaction takes place.

A sublimer is introduced into the reaction vessel for the delivery of solids. The substance may also be supplied dissolved in an inert solvent (C_{10-12} saturated hydrocarbons, etc.[10,19]).

4. Isolation of Organometallic Compounds Formed by Direct Synthesis

Methods of isolation depend on the nature of the compound obtained. Certain structural units should therefore be provided in the apparatus.

Volatile reaction products distil from the reaction vessel into a trap. For such purposes the easily detachable vessel is usually disconnected from the vacuum system and connected to another system, into whose trap the reaction product distils. Equipment fitted with a parallel evacuation line from the reaction vessel may also be used: this line is used for distilling off products while the main vacuum line is closed.

Use of such a system to isolate less volatile products is complicated by their condensation in the vacuum tubes and taps. An interchangeable flange with a receiver ("finger") cooled in liquid nitrogen can be employed for this purpose. When synthesis is complete, the main flange is replaced by the flange with the cooled receiver, on whose surface the reaction products sublime from the walls of the reaction vessel.

Various chemical reactions can be conducted at either room or low temperatures in order to isolate certain organometallic compounds. Diarenechromium complexes, for example, can be oxidised in the presence of water to the diarenechromium hydroxides, which can then be converted into the iodides or into neutral complexes[29,30]. Many examples have been reported of the isolation and proof of formation of unstable products of the cocondensation of atomic metals with organic compounds. The isolation of organometallic compounds RMHal (where M = Ni, Pd) as adducts with phosphines $RMHal.2PR_3$ is typical of such reactions.

To prove the formation of unstable compounds increasing use is being made of the spectroscopic recording (directly on the cooled caesium iodide window of the infrared spectrometer) of compounds formed by the low-temperature cocondensation of metal vapours with organic and inorganic substances[41,52,53].

V. POSSIBILITIES AND PROSPECTS

In the near future the technique of low-temperature cocondensation should take its place in chemical laboratories. It provides unusual opportunities for obtaining Grignard reagents by the cocondensation of magnesium vapour with halogenated organic compounds, and also for preparing an especially active magnesium mass by cocondensation with an inert solvent. Such a mass will give Grignard reagents with the most inert halogenated aromatic compounds. For example[24] the cocondensation of magnesium vapour with oxolan forms a complex that can be used for the synthesis of Grignard reagents:

$$\mathrm{Mg + Oxol} \xrightarrow{196^\circ\mathrm{C}} [\mathrm{Mg.Oxol}]- \left| \begin{array}{l} \xrightarrow{C_6H_5Cl;\ 35^\circ C} C_6H_5MgCl\ (80\%) \\ \xrightarrow{C_6F_5Br;\ 30^\circ C} C_6F_5MgBr\ (80\%) \\ \xrightarrow{CF_3Br;\ 30^\circ C} CF_3MgBr\ (1\%) \end{array} \right. \quad (36)$$

.

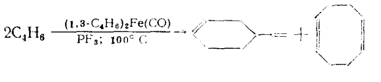
It is of practical interest to prepare a similar active mass of nickel. Thus the cocondensation of nickel vapour with oxolan produces a stable adduct, which is a very good reagent for binding alkyl halides[24,41,42]:

$$2C_3H_5Br + \text{Ni-Oxol} \xrightarrow{40° C} C_3H_5{-}C_3H_5 + NiBr_2 \tag{37}$$

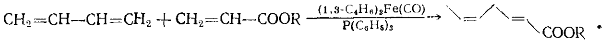
$$2C_6H_5CH_2Cl + \text{Ni-Oxol} \xrightarrow{40° C} (C_6H_5CH_2)_2 + NiCl_2\ . \tag{38}$$

Such solvate complexes of metals are only now beginning to be investigated, but the results already obtained are extremely encouraging.

Complexes formed in cocondensation with atomic metals are often good catalysts for various processes. In the presence of phosphines at 100°C, for example, $(1,3\text{-}C_4H_6)_2.$ $.FeCO$[13] catalyses the dimerisation of dienes and other reactions:



(39)



. (40)

Extremely promising and interesting work has been done[96, 97] on the oligomerisation of butadiene catalysed by products of the cocondensation of vapours of transition metals—titanium, nickel, chromium, manganese, iron, cobalt, vanadium—with butadiene in benzene or toluene in the presence and in the absence of dimeric diethylaluminium chloride. With titanium and iron in the presence of $[(C_2H_5)_2AlCl]_2$ oligomerisation involved 100% conversion; nickel, chromium, vanadium, and manganese also showed great catalytic activity (respectively 90%, 60%, 43%, and 40%); but cobalt was relatively inactive (10%). On oligomerisation in the absence of aluminium complex the greatest catalytic activity was developed by iron, cobalt, nickel, and chromium (90%, 88%, 75%, and 62% respectively), whereas titanium was inactive (10%).

A simple and perhaps more economic process—cocondensation of metal vapours with organic compounds—may be used to prepare catalysts[97]. Titanium can be vaporised by an electron gun at a rate of 70 kg h^{-1}, which makes it possible to produce the catalysts on an industrial scale[98].

Direct synthesis enables especially pure organometallic compounds to be obtained. Thus whereas the usual Fischer preparation of bisethylbenzenechromium yields many homologues with different numbers of alkyl substituents, for example, the cocondensation of chromium vapour with ethylbenzene gives the individual compound bisethylbenzenechromium[99], which is very important in the use of organochromium compounds to obtain chromium films. The technical process requires substances of constant characteristics—boiling point, vapour pressure, viscosity, density, etc.—and use of this method enables standard substances to be obtained for the analysis of various mixtures of organometallic compounds, as well as for obtaining accurate spectral and other characteristics of particular compounds.

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New Heterochain Polymers Based on Cyclic Imides of Carboxylic Acids

I.A.Arkhipova, B.A.Zhubanov, and S.R.Rafikov

Results are given for the use of cyclic imides of carboxylic acids and monomers for new thermostable polyimides and polyamides. Migration copolymerisation, polycondensation, and cycloaddition of imides of aliphatic, aromatic, and unsaturated structure are discussed. A list of 159 references is included.

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I. INTRODUCTION

Anhydrides of di-, tri-, and tetra-carboxylic acids are used as starting materials for the synthesis of most thermostable polyheteroarylenes[1-3]. Use of these monomers in reactions with aromatic di- or tetra-amines yields processable polymers resistant to chemicals and radiation, which withstand prolonged heating to 300°C. However, the preparation and especially the purification of these anhydrides is associated with several difficulties[4]. Existing methods of obtaining polymers from them also have their defects[5], primarily the hydrolytic instability of the polymers formed in the first stage, as well as the complexity of achieving 100% cyclisation in the second stage. The search for other monomers structurally analogous to anhydrides and the development of new methods for synthesising thermostable heterochain polymers are extremely urgent tasks.

Cyclic imides of carboxylic acids are of definite interest in this connection[6]. Effective procedures for their synthesis by the vapour-phase oxidative ammonolysis of alkylbenzenes have been developed recently[3,7,8]. Good yields and ease of purification guarantee important advantages in comparison with anhydrides.

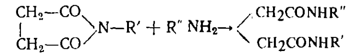
In the present Review we have attempted to summarise examples of the use of such monomers, describe new reactions in which they are used, and report the properties of the resulting polymers.

II. POLYCONDENSATION OF CYCLIC IMIDES WITH AMINES INVOLVING CLEAVAGE OF THE IMIDE RING

It has long been known that cyclic imides of carboxylic acids are able to react with several nucleophilic compounds. Until recently, however, these reactions were not studied in relation to polymer chemistry. Many investigations during the past 10–15 years have shown a promising future for the use of these reactions in synthesising macromolecular compounds. Amines are active nucleophilic components, undergoing aminolysis with imides to give diamides.

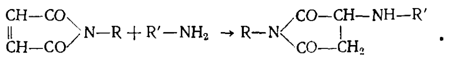
1. Aliphatic Imides

The first systematic investigation of the interaction of aliphatic imides with amines was undertaken by Sheremet'eva and her coworkers during the 1960s. Taking succinimides as examples, they showed[9] that amines in alcoholic solutions in the cold produce cleavage of the imide ring with formation of corresponding mono- or di-substituted diamides:

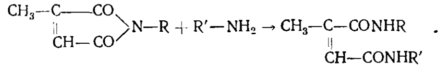


$R' = H, CH_3, C_6H_{11}$, [illegible] = Alk or cycloAlk .

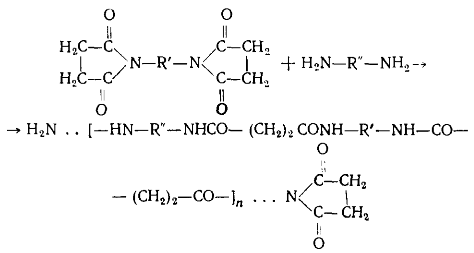
Imides of unsaturated dicarboxylic acids—maleic, citraconic, itaconic—may react differently with amines according to the conditions[9-11]. In anhydrous organic solvents only addition of ammonia and amines at the double bond takes place, with formation of corresponding derivatives of aspartic acid:

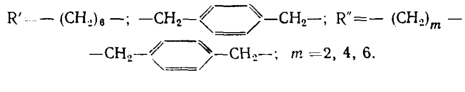


An aqueous solution of an amine causes aminolysis with formation of diamides and preservation of the double bond:



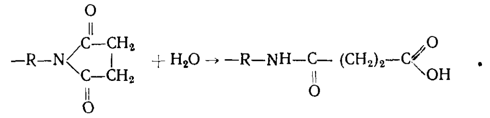
Polymers varying in chemical structure and properties can be obtained by applying these reactions to difunctional compounds. Sheremet'eva et al. were the first to show[12] that linear polyamides can be obtained by the aminolysis of disuccinimides:



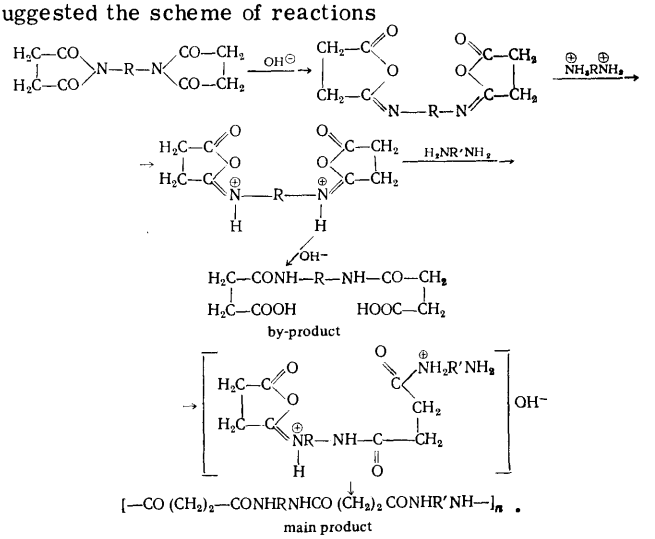


The reaction is conducted under mild conditions, in the cold with prolonged standing of solutions or suspensions of the imides with the amines in the presence of water in such solvents as dioxan, methanol, etc. Polyamides of molecular weight 16 000–20 000 are thus obtained. Reaction does not take place in dry organic solvents even after boiling for many hours[13].

Bisimides of glutaric, aspartic, and unsaturated acids have also been used as initial monomers in this reaction[14]. Mixed polyamides are obtained from bisimides and bisamines containing substituents R′ and R″ differing in structure. Conducting the reaction at room temperature eliminates transamidation and will yield mixed polyamides of strictly specified, regular structure, in which the hydrocarbon fragments R′ and R″ are arranged in a definite sequence in the macromolecule. Termination of the growing polymer chain may result from hydrolysis:

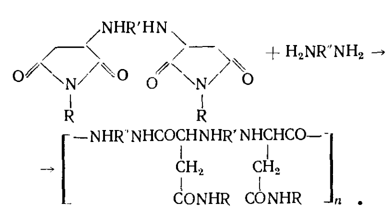


A comparative kinetic investigation of aminolysis and hydrolysis was made in the case of the action of amines on the hexamethylenebisimides of succinic and glutaric acids in order to determine the quantitative relation between these reactions[15]. For each of the bisimides the rate of aminolysis is several times greater than the rate of hydrolysis, and bisglutarimides are hydrolysed appreciably more rapidly than are bissuccinimides. Both processes—aminolysis and hydrolysis—are catalysed by hydroxide ions. The quantitative relation between hydrolysis and aminolysis depends on the pH. With succinimides both processes are second-order reactions with respect to the hydroxide ion, whereas with glutarimides they have the first order. The kinetic results obtained for succinimides suggested the scheme of reactions



Water is assumed[15] to activate both initial components. Amino-groups are converted into ammonium ions, while bisimides isomerise under the influence of hydroxide ions into bisisoimides. Azomethine groups are then protonated by the transfer of protons from ammonium ions. Under the influence of nucleophilic attack by the amine (in the main reaction) or by hydroxyl (in the secondary reaction of hydrolysis) the carbon–oxygen bond in the isoimide ring undergoes fission with formation of the main product and a by-product.

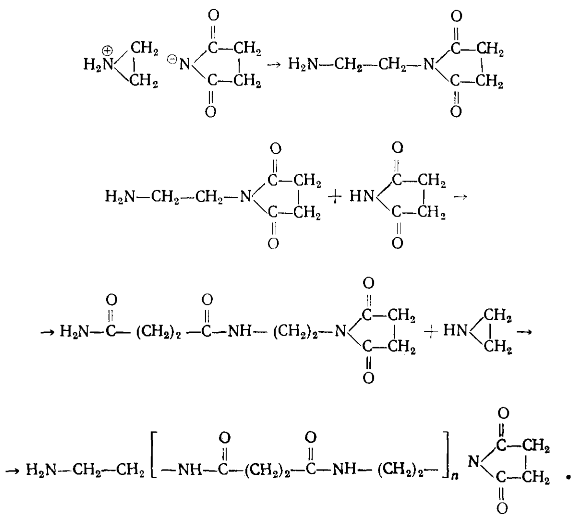
Bisimides of aspartic acid have also been used as initial monomers[16,17]:



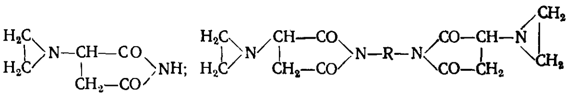
At room temperature they react with bisamides only on the addition of 20–30% of water to the solution. When the water content is increased to 50%, the viscosity of the resulting polymer is lower owing to chain termination by hydrolysis of the imide rings. Reaction does not take place in solutions of anhydrous organic solvents; but at higher temperatures (50–100 °C) the polymer is formed even without the addition of water. The resulting polyamidoimides contain secondary amino-groups in the chain, which strengthen the basic character of the polymer, with consequent improvements in its solubility and its dyeability by acid dyes, while the film- and fibre-forming properties are maintained.

The aminolysis of imides by amines has been used in several other cases. This reaction forms the basis of a process for obtaining crystalline polyamides distinguished by enhanced thermal stability resulting from the regular arrangement of amide groups[18]. The initial monomers are bissuccinimides and aliphatic or aliphatic–aromatic diamines, which are heated in a sealed ampoule at 150–200 °C for 1–5 h.

2,4- and 6,4-Nylons have been obtained by the action of ethylenediamine on ethylene-*NN′*-bissuccinimide and of hexamethylenediamine on hexamethylene-*NN′*-bissuccinimide respectively in a nitrogen atmosphere in a sealed ampoule at 200 °C.[19] Polyamides of high molecular weight have been obtained also[20] by the aminolysis of imides by secondary amines. Thus polyethylenesuccinamides of specific viscosity 0.28 dl g^{-1}, beginning to decompose at 290 °C, result from the interaction of succinimides with aziridine in the melt or in solution at 170 °C. The reaction was assumed[20] to involve formation of an ion-pair comprising an aziridine cation and a succinimide anion:



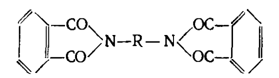
In order to combine imide and imine functional groups in the same molecule, 3-aziridin-1′-ylsuccinimide and 3,3′-diaziridinylbissuccinimides



have been prepared by the action of aziridine on maleimide and *NN*′-bismaleimides respectively. These monomers polymerise with cleavage of the imide and imine rings in the melt at 125°C to form cross-linked polymers that decompose at 300°C. Aminolysis of the imide ring has been used also to cross-link polymaleimides by treatment with aziridine or a diamine[21]. The imide ring is thus opened, and the resulting amide bonds promote formation of a three-dimensional structure in the polyamidoimide.

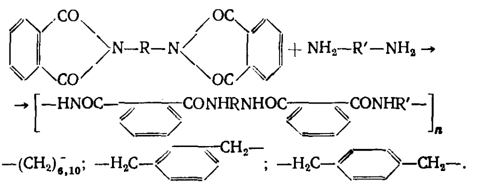
2. Aromatic Imides

Aromatic imides have also been used during recent years as initial monomers in the reactions of bisimides and bisamines involving cleavage of the imide ring. Investigations have been made[22–24] on the action of aliphatic and aliphatic–aromatic amines on *NN*′-disubstituted bisphthalimides



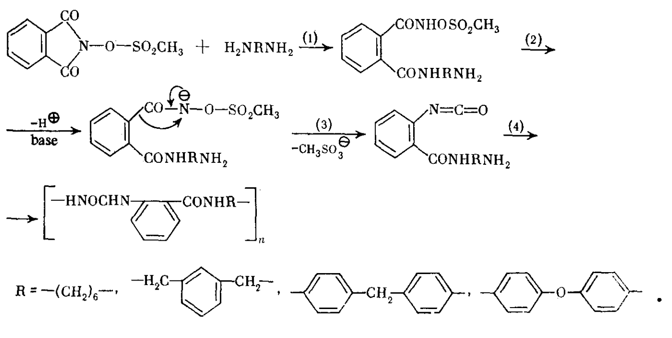
$R = -(CH_2)_n-;\ -m\text{-}C_6H_4-;\ -p\text{-}C_6H_4-;\ m\text{-},\ p\text{-}(CH_2)_2C_6H_4;\ n = 2,\ 4,\ 6.$

Reaction does not take place in water or in aqueous alcohol. In dry organic solvents at 20–95°C polyamides are formed:



The yield and the viscosity of the polymers depend on the nature of the hydrocarbon substituent attached to the nitrogen, the structure of the initial bisamine, and reaction conditions. Bisimides of aromatic or aliphatic–aromatic diamines proved relatively inactive: only oligomeric amides were obtained, and in some cases formation of an amide bond was not observed at all. Alkylenebisphthalimides are considerably more reactive: they react with aliphatic bisamines under homogeneous conditions—dissolved in a mixture of chloroform and alcohol at room temperature or in dimethylformamide (DMF), at 70°C (with 30% solutions in 70 h)—to form polymers of maximum viscosity 0.18 dl g^{-1} in ~40% yield. Under heterogeneous conditions—in suspension in toluene—polyamides of maximum viscosity 0.3 dl g^{-1} can be obtained in ~60% yield.

The presence of strongly electron-accepting substituents attached to the imide nitrogen tends to activate phthalimides towards aminolysis[25,26]. In particular, under mild conditions *N*-methanesulphonyloxyphthalimide[25] reacts both with aliphatic and with aromatic diamines with cleavage of the ring. The reaction is assumed to involve the four stages of (1) nucleophilic attack on the carbonyl by the amine, (2) removal by a base of a proton from the *O*-sulphonylhydroxamic acid, (3) removal of a methanesulphonate anion with subsequent rearrangement, and (4) addition of an amino-group to the isocyanate:



The reaction takes place in the presence of triethylamine or pyridine in *N*-methylpyrrolidone solution at room temperature to give polyphenyleneamidoureas in high yields (94–99%) but of comparatively low viscosity (0.12–0.34 dl g^{-1}), which may be due to chain termination as a result of secondary intramolecular cyclisation with formation of quinazolinedione. The unsymmetrical structure of the polymer chains is responsible for the high solubility of the polyamidoureas and their relatively low softening point (143–261°C).

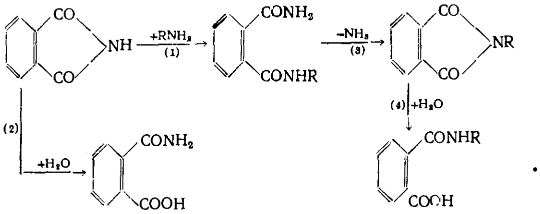
In contrast to *N*-substituted phthalimides, from which linear polyamides are obtained, aminolysis of the imides of aromatic tetracarboxylic acids permits the synthesis of cyclochain polymers, in particular polyimides.

Model monofunctional compounds (phthalimide, 4-cyanophthalimide, trimellitimide, etc.) have shown[27,28] that aminolysis does not occur under mild conditions in anhydrous organic solvents (dioxan, alcohol, DMF, acetone) at 5–20°C. Yet treatment of suspensions of imides with a solution of an aliphatic or an aliphatic–aromatic amine in water or a 1 : 1 mixture of water with an organic solvent leads to rapid interaction of the initial components. The yield of solid products of aminolysis is ~90% for all the imides investigated. From the aqueous filtrate 5–10% of amido-carboxylic acids can be isolated, whose formation indicates secondary hydrolysis of the initial imide ring. Unchanged initial imide is absent from the solid products of aminolysis, the conversion products being a mono-*N*-substituted *o*-bisamide and an *N*-substituted imide. For example, interaction of phthalimide with benzylamine yields *N*-benzylphthalimide and the monobenzylated bisamide of phthalic acid, forming respectively 30 and 70 wt.% of the mixture.

From this it may be assumed that the main reaction leads to subsequent partial cyclisation of *o*-bisamide groups with evolution of ammonia and formation of imides. Indeed, if an aqueous suspension of chemically pure monobenzylphthalamide is kept at 20°C for a few hours, *N*-benzylphthalimide is obtained. Brief (30–90 min) treatment of bisamides with hot water gives the same result. Yet boiling a bisamide in such organic solvents as dioxan, benzene, and pyridine did not result in cyclisation. Nor did heating the dry bisamide at 100°C for several hours produce any chemical change. Cyclisation is observed only above 150°C.

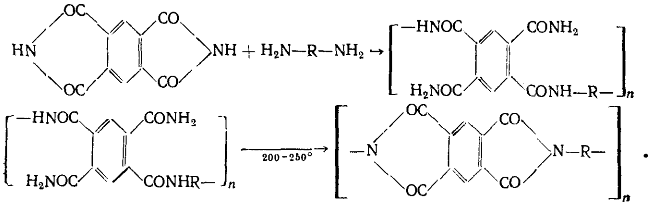
After being heated at 170–200°C for 1 h, bisamides are converted quantitatively into *N*-substituted imides. When *o*-bisamides are boiled in water for the same time, the yield of cylised products is only 50–70% (depending on the nature of the initial bisamide). Up to 50% of ammonium o-amido-carboxylates, products of the hydrolysis of N-substituted imides, then accumulate in the aqueous filtrate[27].

Thus the reaction between an aromatic imide and an aqueous solution of an aliphatic or an aliphatic-aromatic amine can be written



The main reaction of aminolysis (1) is accompanied by slight hydrolysis of the initial imide ring (2). The N-substituted o-bisamides formed in the main reaction are partly cyclised to N-substituted imides (3). The ammonia thus evolved promotes partial hydrolysis of N-substituted imide rings to amido-acids (4). Under the given conditions the main reaction—aminolysis (1)—occurs rapidly and constitutes 90–95%, while the yield of secondary hydrolysis products in reactions (2) and (4) is small, totalling <10%. This enabled the reaction to be extended to difunctional compounds.

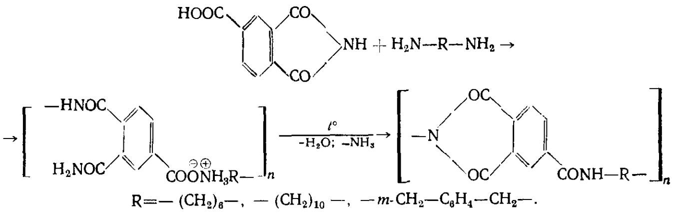
Linear polyimides are obtained[29-31] when the bisimides of pyromellitic and benzophenonetetracarboxylic acids are used as monomers with such bisamines as hexamethylenediamine, xylylenediamines, and bisaminomethylcyclohexane. The reaction takes place in two stages:



The prepolymers formed in the first stage are white powders soluble in strong mineral acids and containing polyamidoamides in the main structure. The infrared spectra of the polymers and investigations on model compounds show that the macromolecule contains also imide rings and salt groups. The first stage occurs at room temperature under heterogeneous conditions, in aqueous suspension. The reduced viscosity (measured for 0.5% solutions in concentrated sulphuric acid at 20°C) for the polyamidoamide from hexamethylenediamine and pyromellitimide was respectively 1.22, 1.08, and 0.91 dl g^{-1} on preparation in water, a 1 : 1 mixture of water and DMF, and a 1 : 1 mixture of water and ethanol, and did not exceed 0.04 dl g^{-1} in dry DMF, ethanol, or dioxan.

In the second stage imidisation occurs in the solid phase at 200–250°C. Cyclodeamination of polyamidoamides takes place more rapidly and at a lower temperature than cyclodehydration of the corresponding polyamido-acids. Polymers obtained from bisimides are therefore distinguished by greater completeness of cyclisation, and surpass in thermal stability polyimides based on analogous bisanhydrides[31]. The cyclised polyimides are insoluble and infusible heat-resistant dielectrics, which begin to decompose at 300–350°C.

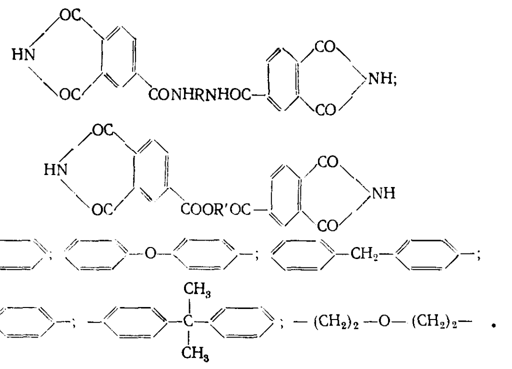
Soluble linear polyamidoimides can be obtained from trimellitimide as initial monomer treated with bisamines under analogous conditions[32]. In this case the first stage, conducted in aqueous solution at room temperature, gives oligomeric products containing amide, imide, and salt groups in the chain; in the second stage these products are heated in the melt at 200–250°C, when the salt and o-bisamide groups undergo polycondensation and cyclodeamination with the liberation of water an ammonia respectively to form polyamidoimides:



The resulting polymers, having $[\eta] = 0.40-0.75$ dl g^{-1}, are soluble in cresol and sulphuric acid, and soften at 210–245°C.

Polymers of analogous structure with $[\eta] = 0.08-0.15$ dl g^{-1} could be obtained in a single stage by the action both of aliphatic and of aromatic bisamines (hexamethylenediamine, ethylenediamine, bis-p-aminophenyl ether, diphenylmethane-pp'-diamine) on trimellitimide in DMF, dimethylacetamide (DMA), or cresol solution at the boiling point with azeotropic removal of the water liberated[33]. The melting points of the polymers vary from 170 to 340°C depending on the structure of the initial bisamine. Thermogravimetry in a stream of nitrogen indicates that decomposition begins at ~490°C.

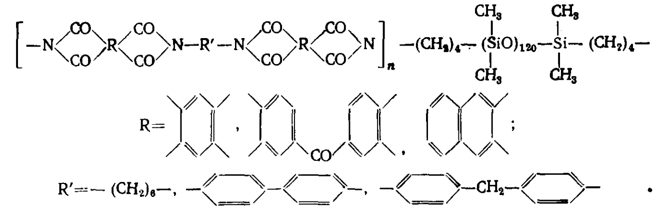
Polymers have been obtained under similar conditions from the bistrimellitimides[34]



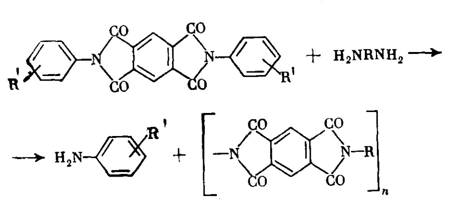
They have $[\eta] \leqslant 0.1$ dl g^{-1}, which indicates that the functional groups are relatively inactive under the given conditions. The polyetherimides, polyesterimides, and polyamidoimides formed are ordered polymers[34,35]. Regular arrangement of the structural units of macrochains ensures stronger intermolecular interaction between polar groups. This is why the ordered polymers have higher melting points and lower solubilities than similar polymers based on trimellitimide. However, ordered polymers differ little in thermal stability from unordered copolymers[35].

Block copolyimides of high molecular weight and viscosity ~1.0 dl g^{-1} have been obtained[36] by the stepwise reaction of aromatic bisimides first with aliphatic or aromatic bisamines and then with polyorganosiloxanediamines. The reaction takes place in solution in hexamethylphosphoramide (HMPA) or other strongly polar solvent (tetramethylurea, dimethyl sulphoxide (DMSO), N-methylpyrrolidone) with the monomers held for a long time (10–20 h) first at

20 and then at 70–80°C. This involves successive addition of the amine with cleavage of the imide ring and then cyclodeamination. The products are film-forming polyimides

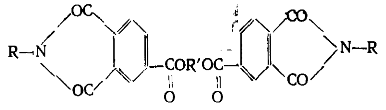


Imido-amine exchange between an *NN′*-diarylated pyromellitimide and an aromatic bisamine probably also occurs by a mechanism of successive opening and closing of the imide ring[37]. The reaction takes place in the melt at 250–300°C, with liberation of the corresponding aromatic amine and formation of an insoluble, infusible polyimide:



$R = Ar \quad R' = -OCH_3, -OC_2H_5, -OH, Hal$.

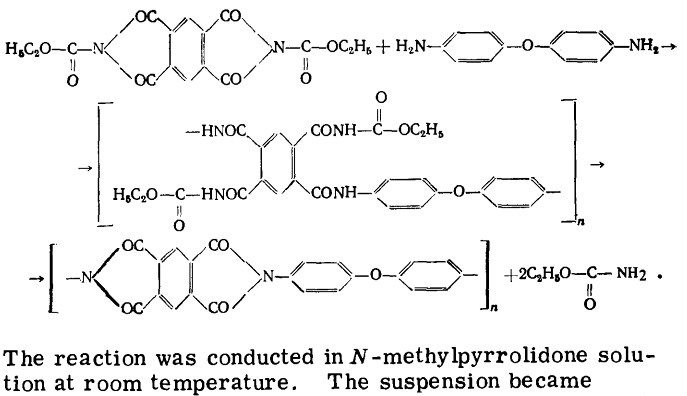
The same reaction has been applied under analogous conditions to diester-bistrimellitimides[38,39]



$R = Alk, Ar; \ R' = C_{6-30}\cdot Ar$.

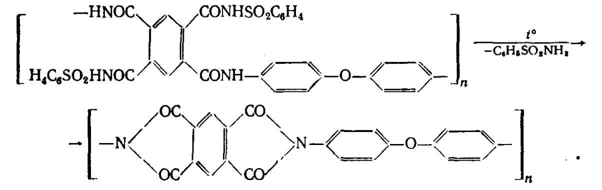
These monomers react in the melt with aliphatic, aromatic, or siloxane diamines to form soluble, fusible linear polyesterimides. The use of metals of Groups I and II–Vb or their oxides, hydroxides, imides, or salts as catalysts in this reaction enables polymers of higher molecular weight to be obtained.

The introduction of strongly electron-accepting substituents into the imide group enables the reaction to be conducted under milder conditions with formation of an easily processable and readily soluble polyamide as prepolymer. Such *N*-substituted bisimides include diethyl pyromellitimide-*NN′*-dicarboxylate[40–42], which has been subjected to two-stage polycondensation with diamines:

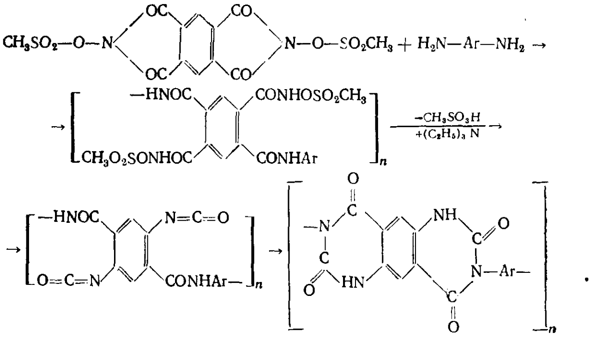


The reaction was conducted in *N*-methylpyrrolidone solution at room temperature. The suspension became homogeneous after being stirred for 1 h, but the viscosity continued to increase for 5 days, reaching 0.9 dl g^{-1}. A strong, flexible film was cast from the resulting polyamide solution, and was heated in a vacuum above 240°C for 5 h to form a polyimide.

A more vigorous reaction takes place between *NN′*-diphenylsulphonylpyromellitimide and bis-*p*-aminophenyl ether[43]. In solution at room temperature a polyamide of reduced viscosity up to 0.9 dl g^{-1} is formed within 30–60 min. A solution of a polymer (in contrast to solutions of polyamido-acids) has a stable viscosity, but even at 20°C such a polyamide gradually cyclises in solution, a process considerably accelerated by the presence of water. Complete conversion into the polyimide occurs when the polyamide films are heated at 160°C for 10 min. Cyclisation is accompanied by the separation of benzenesulphonamide as a by-product:



An analogous reaction between *NN′*-dimethanesulphonyloxypyromellitimide and aromatic bisamines yields new polymers, containing quinazolinedione rings in the chain[44]:



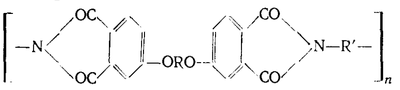
The reaction is conducted in *N*-methylpyrrolidone solution at room temperature in the presence of tertiary amines, which promote formation of the polyamidoisocyanate and subsequent isomerisation cyclisation. The polymers are obtained in theoretical yield with a specific viscosity of 0.25 dl g^{-1}. The comparatively low viscosity is due to separation of the polymer from the solution at an early stage. The resulting polypyrimidoquinazolinetetraones are soluble only in strong mineral acids, and are stable up to 400°C.

The above examples show that cyclic imides of aliphatic, unsaturated, and aromatic carboxylic acids are able to undergo ring cleavage on reaction with diamines. The activity of the monomers in this reaction is determined by their chemical structure and by the reaction conditions. With strongly basic aliphatic amines reaction takes place even at room temperature, when a necessary condition is often the presence of water, which probably activates both monomers. Linear polyamides are then formed from imides of aliphatic and unsaturated acids. Imides of aromatic tetracarboxylic acids yield polyamides containing *ortho* to the amide bond primary or secondary amide groups capable of cyclisation with the separation of a by-product of low molecular weight and the formation of linear polyimides. Under more severe conditions reaction takes place also with the less basic aromatic diamines, when a polyimide is obtained without separation of the prepolymer.

III. POLYCONDENSATION WITHOUT CLEAVAGE OF THE IMIDE RING

Recently cyclic imides of carboxylic acids have begun to be used also in polycondensations. Aromatic bisimides containing hydroxyl, carboxyl, and chlorocarbonyl as reactive functional groups are often employed as monomers in polyamidation and polyesterification with bisamines, bisisocyanates, and phenolic diols. Sometimes different types of functional groups are combined in the same molecule, and homopolycondensation is effected. These reactions enable us to obtain in a single stage polyimides containing also other hetero-bonds (amide, ester, etc.), in which unstable uncyclised *o*-amido-acid units are absent. The present Review omits many examples of such reactions reported for various imides of tri- and tetra-carboxylic acids, which have been discussed previously[3], and dwells only on comparatively unknown reactions.

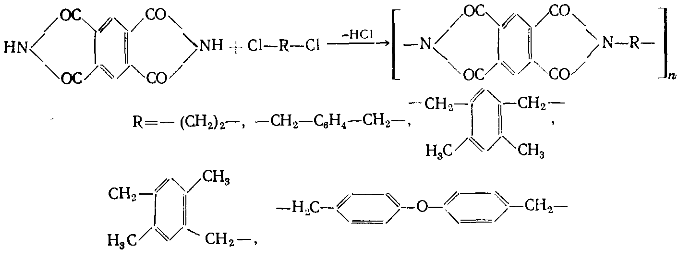
As already remarked, until not long ago imides of *o*-dicarboxylic acids were not used for the preparation of polymers. Several recent patents reveal the possibility of applying polycondensation to such monomers in order to synthesise the polyetherimides



R = Arylene; R′ = Arylene, Alkylene .

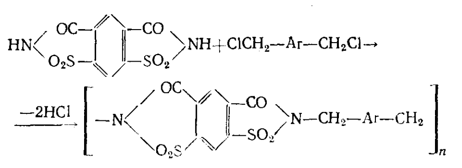
Bisnitrophthalimides are condensed with alkali-metal derivatives of dihydric phenols[45,46] or metal salts of aromatic dicarboxylic acids[47]. The reaction takes place in solution in DMF at 50°C. Bischlorophthalimides[48], bisfluorophthalimides[49], and bischloronaphthalimides[50] react similarly with alkali-metal bisphenoxides in polar solvents or their mixtures with aromatic hydrocarbons at high temperatures.

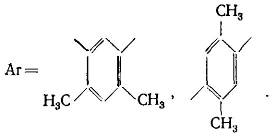
Polycondensation is applied also to unsubstituted imides of aromatic tetracarboxylic acids. Nishizaki and Fukami[51,52] were the first to suggest condensing the di-imide of pyromellitic acid with dihalides by Gabriel's reaction as a new method of synthesising polyimides:



Reaction occurs in the presence of basic catalysts in solution at 70°C to give a 50–80% yield of the polymer.

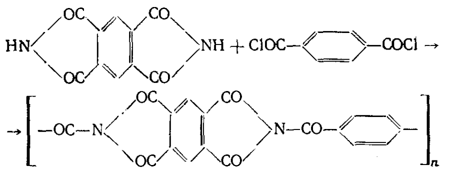
An analogous reaction has recently been reported between aromatic bischloromethyl derivatives and the bisimide of 4,6-disulphoisophthalic acid[53,54]:





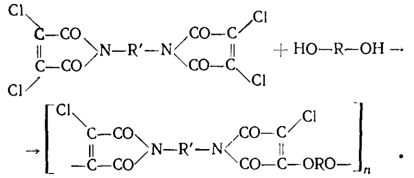
Polar amide solvents were used at the boiling point. Soluble polyimides having a specific viscosity of 0.2 dl g^{-1} were obtained after 5 h.

Imides of aromatic and alicyclic acids are capable also of polycondensation with chlorides of aliphatic and aromatic dicarboxylic acids[55]:

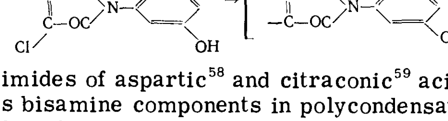


Reaction takes place in the presence of a catalyst—triethylamine, pyridine, aniline, copperII chloride, cobalt naphthenate, an organic compound of tin, or an alkali-metal salt of an organic or an inorganic acid—in solution at 80–200°C. The yield of polyimides exceeds 90%, and their specific viscosity 0.9 dl g^{-1} (for a 0.5% solution in concentrated sulphuric acid). The thermal stability of the polymers is above 350°C.

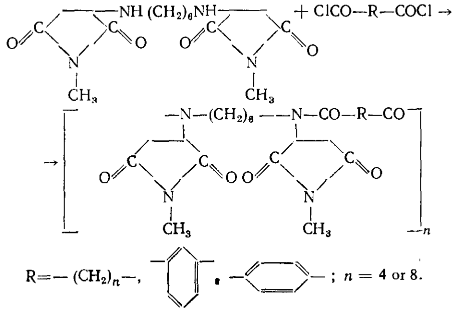
Imides of unsaturated and aliphatic acids undergo polycondensation by means of various functional substituents attached to carbon atoms. Thus the reaction of *N*-aryl-3,4-dichloromaleimides with phenols forms the basis of the synthesis of new polyethermaleimides[56,57]:



Use as initial monomers of 2,2-diphenylpropane-*pp*′-diol and a bisdichloromaleimide together with diphenylmethane-*pp*′-diamine gave a high yield of a polymer having specific viscosity 0.47 dl g^{-1}, capable of forming strong elastic films stable in nitrogen and in air at temperatures above 300°C. The 3,4-dichloro-*N*-*m*-hydroxyphenylmaleimide synthesised was capable of homopolycondensation:



Bisimides of aspartic[58] and citraconic[59] acids can be used as bisamine components in polycondensation with chlorides of dicarboxylic acids. Good yields are obtained of polyamides in which all hydrogen atoms in the amino-group are replaced by imide rings capable of various conversions[60]:



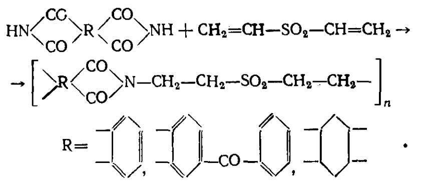
Complete aminolysis of imido-groups can be achieved by methylamine or they can be hydrolysed with alkali[60]. The main chain of the macromolecule does not break down, and new water-soluble polymers are formed.

IV. MIGRATION COPOLYMERISATION INVOLVING THE IMIDE RING

Since the nitrogen atom in an imide of a di- or tetracarboxylic acid is adjacent to two strongly electron-accepting carbonyl groups, the proton attached to the nitrogen atom is mobile. This enables unsubstituted amides to undergo proton-transfer reactions, so that migration copolymerisation can occur without cleavage of the imide ring.

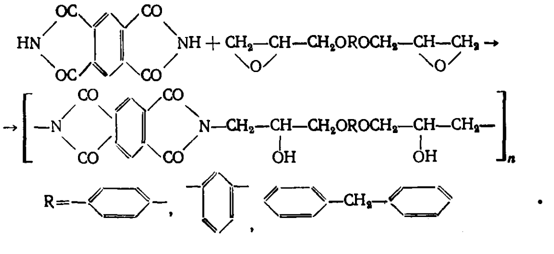
Among such reactions are the migration copolymerisation of unsubstituted bisimides of aromatic[61] and alicyclic[62] acids with dienes containing two active double bonds. Examples of such dienes that are used may contain α to a double bond a carbonyl group or an aromatic ring capable of activating it (e.g. divinylbenzene, diacrylates, vinyl esters of dicarboxylic acids, etc.). Reaction takes place in any suitable solvent at 80–120°C in the presence of a basic catalyst—an alkali or an alkaline-earth metal or its alkoxide, or a Grignard reagent—the quantity of which may vary from 0.0001 to 0.5 equiv. Polymers of high melting point, having specific viscosities of 0.35–0.65 dl g^{-1}, are formed in ~80% yield.

Russo and Mortillaro[63] suggested the use of divinyl sulphone as copolymerising diene:



The reaction is conducted in the presence of sodium t-butoxide in DMSO, DMF, or pyridine solution at 100°C. Infusible crystalline polymers of viscosity 0.09–0.23 dl g^{-1}, soluble only in concentrated sulphuric acid (in the case of aromatic imides) or in amide solvents (in the case of alicyclic imides), are formed in 50–80% yield. Their thermal stability is ~300°C independently of the structure of the monomer unit.

Linear polyimides containing hydroxyl groups have been obtained[64,65] from bisimides of aromatic tetracarboxylic acids and such diepoxides as the diglycidyl ethers of aromatic diols:



Reaction occurs in the presence of a tertiary amine or a quaternary ammonium salt as catalyst in solution at a high temperature. The yield of the resulting hydroxylated polyimides is 60–86%, with a specific viscosity of 0.1–0.34 dl g^{-1}. The polymers melt at 140–280°C, and vigorous decomposition begins at 300–400°C.

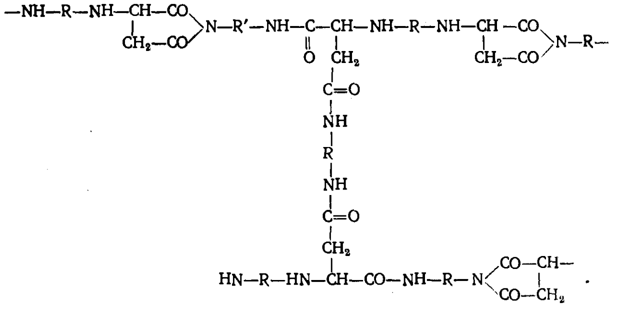
Bisimides of alicyclic tetracarboxylic acids react similarly with aliphatic and alicyclic diglycidyl ethers[66]. This gives oligomers having terminal epoxide groups, which are then hardened with anhydrides of dicarboxylic acids. In the presence of a highly effective catalyst—a chromium tricarboxylate—bisimides of aromatic or alicyclic acids may react also with epoxy-resins to form cross-linked polyimides[67].

V. REACTIONS AT THE DOUBLE BOND IN UNSATURATED IMIDES

As already mentioned, two reactive centres—an imide ring and a double bond—are present in mono- and bisimides of unsaturated dicarboxylic acids. The double bond enables such monomers to undergo several reactions characteristic of alkenes. Disregarding vinyl polymerisation with opening of the double bond by a radical mechanism (since the literature on this topic is vast and requires separate discussion), we shall consider only certain transformations of the double bond of unsaturated imides in migration copolymerisation with nucleophilic compounds and in the Diels–Alder reaction.

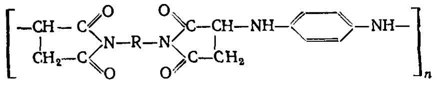
1. Migration Copolymerisation with Amines

In the migration copolymerisation of unsaturated imides with bisamines the chain grows by migration of hydrogen of the imide group to the double bond with the formation of secondary amine units. Polymers were first obtained in this way by Sheremet'eva[14]. When ethylene- and hexamethylene-bismaleimides are treated with such bisamines as phenylenediamine, hexamethylenediamine, ethylenediamine, and piperazine in aqueous alcohol, both reactive centres in the bisimide are involved, and a rubberlike cross-linked polymer is formed, containing imide rings and aspartamide segments in the chain

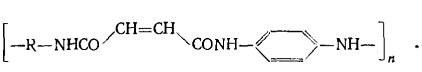


When carefully dried reagents are used in anhydrous organic solvents, the imide ring is preserved and only the double bond is involved. The linear polyaminoimides formed are soluble in several solvents, and have intrinsic viscosities of 0.05–0.18 dl g^{-1}. The molecular weight determined from the terminal amino-groups is 2000–9000.

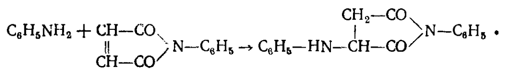
Reaction between dimaleimides and aromatic or aliphatic–aromatic diamines in the melt at 80–200°C yields[68] linear polyimides soluble in concentrated sulphuric acid and HMPA, resistant to abrupt changes in temperature, and beginning to decompose at 400°C. Such polymers comprise 85% of polyaminoimide units



and 15% of units of structure

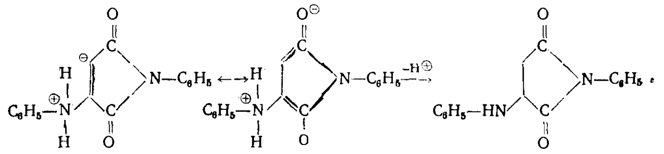


Study of the migration copolymerisation of bisimides of unsaturated acids with bisamines was then developed[69,70] by examining as model reaction the action of aniline on *N*-phenylmaleimide



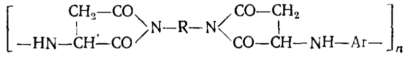
$$C_6H_5NH_2 + \begin{matrix}CH-CO\\ \| \\ CH-CO\end{matrix}\!\!>N-C_6H_5 \rightarrow C_6H_5-HN-\begin{matrix}CH_2-CO\\ | \\ CH-CO\end{matrix}\!\!>N-C_6H_5\ .$$

Since the reaction velocity depends on the polarity of the medium, it was supposed[69,70] that the mechanism involved a charged intermediate product stabilised by the medium:



This mechanism suggests the possibility of acid and base catalysis. Indeed, weak protic acids (acetic, propionic, formic, maleic) exhibit a considerable catalytic effect.

Extension of this reaction to difunctional compounds—bismaleimides and aromatic diamines—yields the polyimides



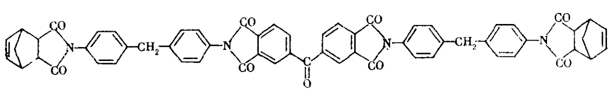
$$\left[-HN-\begin{matrix}CH_2-CO\\ | \\ CH-CO\end{matrix}\!\!>N-R-N<\!\!\begin{matrix}CO-CH_2\\ | \\ CO-CH-NH-Ar-\end{matrix}\right]_n$$

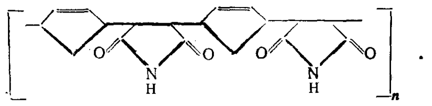
R = Alk, Ar.

Conducting the reaction in the presence of a catalyst—acetic acid—in cresol solution at 100–110°C for 3 days gives polyaspartimides as amorphous compounds softening at 210–300°C (depending on the chemical structure of the initial monomers) and having high melting points[70]. They are soluble in phenolic and amide solvents, their viscosity being $[\eta] = 0.25-0.6$ dl g^{-1}.

Migration polymerisation can be accomplished also in other phenolic solvents[71], benzonitrile, DMF, DMSO, nitrobenzene[72], and various phosphorus-containing compounds[73]. The use has been suggested also of such carboxylic acids as acetic, propionic, trifluoroacetic, formic, etc., which act as both solvent and catalyst[74]. Mineral acids and certain complex compounds may be used as catalysts[75].

Linear polyaminoimides obtained by the migration polymerisation of bisimides with bisamines can be hardened by heat, forming insoluble, infusible polymers of good heat and chemical resistance. The mechanism of thermosetting is not clear, but the presence of terminal amino-groups and double bonds, together with reactive secondary amino-groups and imide rings in the main chain, promotes various reactions—polymerisation, migration copolymerisation at the imide ring or the double bond, as well as other processes governed by the chemical nature of the macromolecular chain—leading initially to branching and then to cross-linking. For example, the oligomeric prepolymer[76] containining tetrahydro*endo*methylenephthalimide fragments as end-groups, is cross-linked on heat treatment at 260–300°C, without the evolution of volatile components. It is assumed that pyrolytic polymerisation takes place by a mechanism opposite to the Diels–Alder reaction, and the final polymer contains the units





Polyaminoimide prepolymers are most often set in the melt at 200–250°C, either in the presence or in the absence of radical or ionic catalysts. Any mono-or poly-functional compounds that react with the resin can be used in the hardening process. Thus 5–95 wt.% of the corresponding monoimides can be introduced[77,78] during setting into oligomeric prepolymers obtained from bisamines with bismaleimides, bistetrahydrophthalimides, or bistetrahydro*endo*methylenephthalimides, their addition lowering significantly the price of the required thermostable polymer. Alkene hydrocarbons or unsaturated ethers[79–81], condensation polyesters containing double bonds[82], epoxides[83], and epoxy-resins[84,85] have also been suggested as copolymerising and cross-linking additives.

The two-stage method, in which a soluble, fusible polyaminoimide obtained in the first stage is subsequently hardened, has proved extremely fruitful, and has led to the appearance of numerous patents claiming either modification of this method or new compositions that can be used as varnishes, glues, laminated materials, moulded articles, etc.[86–90] Thus products of the reaction of bismaleimides, biscitraconimides, bistetrahydrophthalimides, or bisitaconimides with di-, tri-, or tetra-amines (heated to 50–180°C in the absence of a solvent or in a polar solvent) have been proposed[91] for obtaining thixotropic aqueous suspensions of prepolymers. The resulting polymer is suspended in water and used as a paste for various purposes. After additional heat-treatment (at 250°C for 24 h) a glassfibre-reinforced plastic in which the binder is a similar composition based on diphenylmethane-*pp'*-bismaleimide and diphenylmethane-*pp'*-diamine withstands being heated at 250°C for 1000 h, with only a slight decrease in bending strength.

Prepolymers formed similarly by the migration copolymerisation of bismaleimides with bisamines in polar organic solvents can be modified, without isolation from the solutions, by the addition of anhydrides of polycarboxylic acids[92]. Some of the secondary amino-groups of the main polymer chain react, and carboxy-groups are introduced into the side-chain of the polymer. These ensure that the prepolymer becomes soluble in water on addition of a base. Such solutions have been proposed for electrodeposition on metal surfaces. The transparent protective coatings formed after further hardening at a high temperature are strong and chemically resistant.

Not only individual diamines but also oligomeric or polymeric bisamines[93,94], monoamines[95], and even ammonia[96] can be used in migration copolymerisation. The comonomers may be oligoimides[96–98] as well as bisimides. The migration copolymerisation of bisimides with bisamines and hardening are often combined into a single stage. Polymers are thus formed from mixtures of the initial monomers when heated in the melt[99–102]. To facilitate processing and lower the melting point phosphoric esters are sometimes added to the mixture[99,103]. The addition of polymerisation initiators such as dicumenyl peroxide, etc. accelerates cross-linking and lowers the setting temperature.

It must be noted in conclusion that the manufacture of polyaminoimides from bismaleimides and aromatic bisamines has now been established in several countries. On several criteria, including heat resistance, these polymers are little inferior to aromatic polyimides from tetracarboxylic bisanhydrides and bisamines. Yet the technology of their production and processing has several important advantages: as the prepolymers they are stable, and are easily processed by the same technology as for the usual thermosetting plastics; and the shape of articles on hardening is fixed without the evolution of volatile components[104,105].

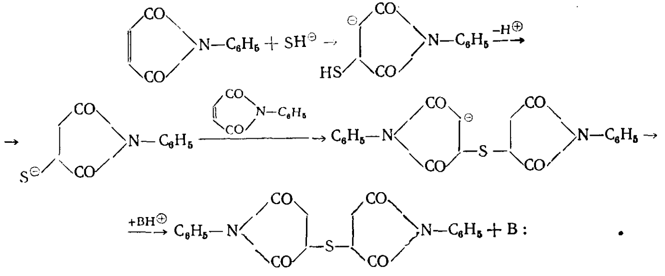
Such a resin is manufactured in France under the trade name Kerimid. Moulding materials such as Kinnel based on it, reinforced with glass fibres, are distinguished by their heat and flame resistance, with great stability towards the action of solvents. They are intended for use in aircraft construction, electronics, and the electronic industry[106-108]. Casting and moulding compositions of self-lubricating type are manufactured, filled with powdered tetrafluoroethylene, molybdenum sulphide, graphite, or carbon fibres. Such compositions possess not only great heat resistance but also low surface friction with insignificant abrasion. At high temperatures these materials surpass steel, light alloys, and titanium in their strength characteristics.

2. Migration Copolymerisation with Other Nucleophiles

Nitrogen-containing compounds other than amines are also used in migration copolymerisation with unsaturated imides, e.g. urea[109], hydrazines[110], dihydrazides[111], bisaldoximes[112-114], and bisimidic esters[115]. Various sulphur-containing compounds—hydrogen sulphide[116], dithiols[117,118], disulphinic acids[119]—are also employed.

Crivello[120] was the first to examine as model reaction the action of hydrogen sulphide on *N*-phenylmaleimide in various solvents, and found the reaction to be instantaneous in solvents of basic character (DMF, DMA, pyridine). If neutral or weakly acid solvents are sued, small quantities of a tertiary amine or other base (B:) must be present as catalyst. Hence it may be concluded that the primary attack on the double bond in the maleimide is initiated by the highly nucleophilic hydrogen sulphide anion, and the mechanism of the reaction can be written

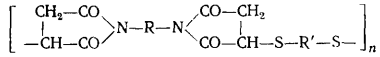
$$H_2S + B: \rightleftarrows BH + SH^{\ominus}$$



The attempt to extend this reaction to difunctional compounds has been unsuccessful: the action of hydrogen sulphide and dithiols on bisdimaleimides in polar organic solvents at room temperature produces rapid gelation. The anionic polymerisation of bisimides initiated by thiolate ions is regarded as a competing reaction leading to cross-linking. However, this side reaction could be effectively suppressed by conducting polymerisation in weakly acid media or by adding to the reaction mixture small quantities (0.5–10%) of protonating agents such as inorganic acids (sulphuric, phosphoric), carboxylic acids (acetic, formic, benzoic), phenols, or various acid salts[116]. Catalytic quantities (0.01–0.001 wt.%) of such tertiary amines as tetramethylethylenediamine, tributylamine, etc. can be used to accelerate the reaction[118].

The reaction can be conducted in the usual organic solvents, in compounds of amide type, and also in aqueous emulsion. In the last case acid and neutral alkali-metal salts are used as catalysts. The most successful media were phenol and cresol, which acted both as solvents and as protonating agents. Thus the action of hydrogen sulphide under these conditions on bismaleimides[120] or oligomeric aminoimides containing two terminal double bonds[121] will give good yields of macromolecular polyimidosulphides, clear fibrous polymers having $[\eta] = 0.1–0.63$ dl g^{-1}, soluble only in highly polar liquids (DMSO, DMA, hexafluoroacetone hydrate) and resistant to the usual organic solvents. They melt at comparatively high temperatures (260–300°C) and are stable up to 325°C.

Replacement of hydrogen sulphide by a dithiol will yield polyimidosulphides having the structure



in which R and R′ are different bivalent organic radicals of aliphatic, aromatic, or heterocyclic type. The properties of the polymers depend on the structure of the main chain. Thus lengthening the segments between two sulphur atoms results in lower melting points and greater solubility of the polymers in the usual organic solvents.

Block copolymers containing polyimidosulphide and polysulphide units can be obtained by using oligomeric polysulphides of molecular weight 2000–8000 as second components in migration copolymerisation with bismaleimides[122,123]. The reaction is conducted in the presence of tetramethylethylenediamine in cresol or its mixture with dichloromethane at 40°C. Polymers containing ≥70% of polysulphides are thermoplastic elastomers; with lower contents of polysulphides they can be regarded as thermoplasts modified with rubbers. The strength properties of the block copolymers deteriorate with increase in the quantity of the polysulphide component, but are little affected by its molecular mass or the nature of the polyimidosulphide block. The thermal stability of the copolymers is determined by that of the polysulphide blocks.

Linear polyimidosulphides obtained by the migration copolymerisation of unsaturated bisimides with sulphur-containing monomers are hardened at 150–300°C either purely thermally or in the presence of organic peroxides.

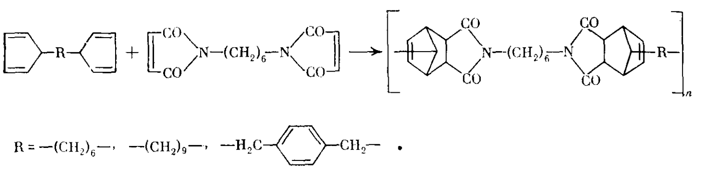
Polyimidosulphides, which are characterised by high mechanical strength and heat resistance, are recommended for the production of electrically insulating films and coatings, moulded goods, packing materials, and gas-separating membranes[117,119,124].

3. Cycloaddition

Reactions involving cycloaddition provide another promising and growing method for using unsaturated bisimides to obtain polyimides of various structures. The literature on this topic up to 1965 was presented in review papers[125,126] and in Korshak's monograph[127]. Therefore we shall discuss in some detail only results that have appeared during recent years.

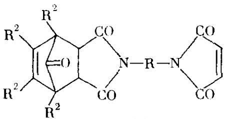
Bismaleimides are successfully used in photochemical homopolymerisation processes involving 2 + 2 cycloaddition, which yields polyimides containing alicyclic units in the chain[128,129], and also as dienophiles in copolymerisation with dienes involving thermal Diels–Alder 4 + 2 polyaddition. The latter type of reaction permits wider variation in the chemical composition and the properties of the polymers, since both cyclic and open-chain dienes can be used. Cyclopentadiene derivatives have been investigated in the greatest detail among diverse diene components. The copolymer of *m*-phenylene-*NN*′-bismaleimide with *p*-xylylenedi-5-cyclopentadiene was first mentioned by Upsom[130], who obtained an insoluble product from the reaction in the mass. Its composition and its insolubility suggest a cross-linked copolymer containing mainly units formed by vinyl polymerisation of the bismaleimide.

Further investigation showed[131] that Diels–Alder polyaddition uncomplicated by 1,2-polymerisation takes place in benzene and DMF solution with the formation of 1 : 1 copolymers:

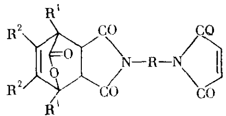


The resulting polyimides probably have relatively low molecular weights, since $[\eta] = 0.1–0.22$ dl g^{-1}, they soften at 110–240°C, and they dissolve in organic solvents. Raising the temperature of the reaction medium leads to the formation of polymers of lower viscosity, which indicates occurrence of the reverse Diels–Alder reaction.

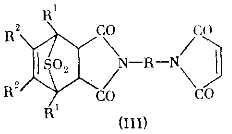
Polyimides of far higher molecular mass were obtained by Kraiman[132,133] and by Chow[134,135], using as monomers adducts of bismaleimides with cyclopentadienone (I), 2-pyrone (II), and thiophen dioxide (III)



(I)

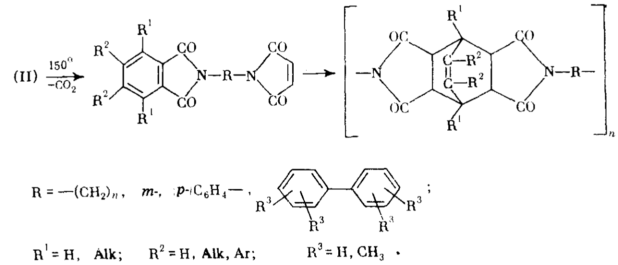


(II)



(III)

Such adducts contain both dienophile and diene reaction centres, but the latter is in an inactive, "protected" state. With rise in temperature either carbon dioxide or sulphur dioxide is evolved from the adducts (I)–(III), and the liberated diene bonds copolymerise rapidly with the dienophile end of the monomer to form a polyimide:



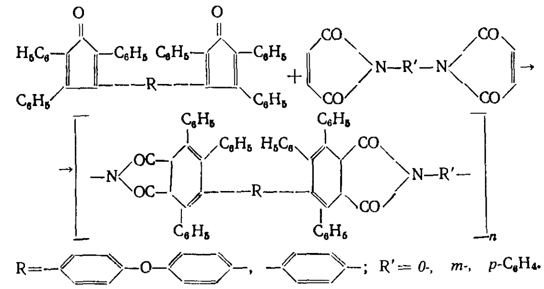
R = —(CH₂)ₙ, *m*-, *p*-C₆H₄—, ;

R¹ = H, Alk; R² = H, Alk, Ar; R³ = H, CH₃ .

The reaction is conducted in a solvent of high boiling point (bromobenzene, a halogenated aliphatic hydrocarbon, 1-chloronaphthalene)[132–135], when macromolecular polyimides having $[\eta] = 2.0$ dl g^{-1} can be obtained in times varying from 20 min to several days depending on the temperature. Under these conditions the Diels–Alder reaction is not complicated by the secondary vinyl-type polymerisation characteristic of free cyclopentadiene.

Polymers which either melt at low temperatures or soften at high temperatures are obtained depending on the nature of the substituent R in the di-imide. The nature of the substituents R¹ and R² in the diene monomer has little influence on the physical properties of the polyimides. The solubility, the high heat resistance, the strength, and the good film-forming and dielectric properties enable the resulting polymers to be used as high-temperature insulating films, fibres, and thermostable and chemically resistant plastics.

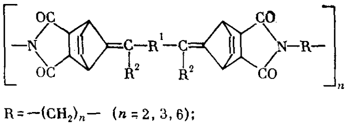
Interesting polyimides, capable of aromatisation, have been obtained from bismaleimides with phenylated derivatives of cyclopentadienone. Model monofunctional compounds[136,137] and monomers[138] have shown that the reaction conforms to the scheme



Polydihydrophthalimides are formed in theoretical yield: The reaction is conducted in boiling chloronaphthalene or trichlorobenzene solution to give maximum viscosities $[\eta] = 0.3–1.0$ dl g^{-1} for various polymers after 1–3 and 18–24 h respectively. The polymers are stable in air up to 300°C. They are dehydrogenated to the corresponding aromatic polyimides by the action of bromine or by heating in nitrobenzene solution. Under these conditions, however, the degree of conversion is probably not very high, since the temperature at which decomposition of the polymer begins has changed little after modification.

Quantitative aromatisation could be accomplished[136,137] by heating a carefully ground specimen of the polymer *in vacuo* at 350°C, when some decrease in viscosity was observed. The resulting polyimides do not lose weight in air up to 530°C: i.e. they are comparable in thermal stability with polyimides based on pyromellitic bisanhydride and aromatic bisamines. In contrast to the latter, however, they dissolve in several organic solvents.

Cyclicdienes other than cyclopentadiene derivatives are also used as monomers copolymerising with bisimides by the Diels–Alder reaction. Thus polyimides of high molecular weight

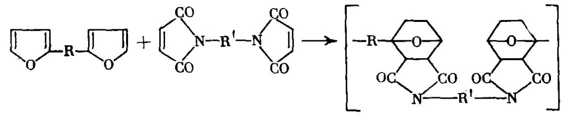


R = —(CH₂)ₙ— (*n* = 2, 3, 6);

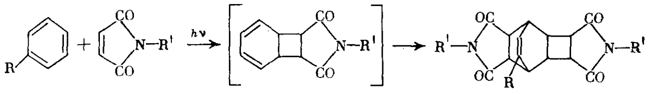
p- or *m*- C₆H₄, *p*-C₆H₄·C₆H₄, *m*-CH₂—C₆H₄—CH₂;

R¹ = Ar; R² = Alk, cycloAlk, Ar

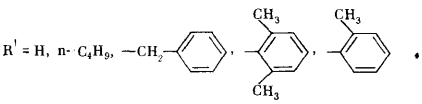
have been obtained[139] by copolymerisation with difulvenes in chloroform, DMF, or *N*-methylpyrrolidone solution at 60–70°C. Berlin et al.[140,141] showed the possibility of using ωω′-difuran derivatives as dienes:



For a long time aromatic compounds were not used as diene components, since it was considered that they were incapable of Diels–Alder condensation. However, later investigations have shown that maleimide and certain of its *N*-substituted derivatives, on exposure to ultraviolet radiation in the presence of a sensitiser, add to benzene and its homologues to form 2 : 1 adducts[142–145]. It is supposed that an intermediate equimolecular adduct formed by photoinitiated 1 + 2 cycloaddition is then involved in Diels–Alder 1 + 4 cycloaddition:

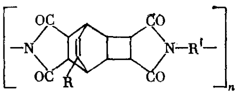


$R = H, C_nH_{2n+1}$ $(n = 1, 2, 10-13)$;



This reaction has recently been extended to bismaleimides to give corresponding macromolecular polyimides. Such polymerisation was first achieved by Stevens and Musa[146,147]. When solutions of various bismaleimides in a mixture of benzene and acetone are exposed in the presence of acetophenone to ultraviolet radiation for 18 h, the polyimides listed in Table 1 are obtained. The yield of polymer obviously depends significantly on the nature of the substituent R in the bisimide: thus the yield is 70–95% in the case of alkylenebismaleimides. The highest yield is observed with R = $[CH_2]_2$. Increasing the number of methylene units in the maleimide bridge lowers the yield, which may be due to intramolecular polymerisation of the double bonds and formation of cyclic bisimides of low molecular weight. If R = C_6H_4, which may be *meta-* or *para*-substituted, the yield of polymer falls to 15–30%. In such molecules the phenyl rings are probably coplanar with the maleimide rings, and this favours the appearance of low excited states which quench the photoexcitation of maleimide. Introduction of an *ortho*-substituent prevents coplanarity, and the yield of polymer then increases to 65–80%. All the polymers obtained begin to decompose at 360°C. Since change in the chemical structure has hardly any effect on the temperature at which decomposition begins, it is assumed[147] that degradation of the polymer chains begins with thermal decyclisation by a reverse Diels–Alder reaction.

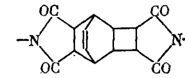
The reaction can be applied also to various homologues of benzene. Thus the use of various alkylbenzenes as comonomers[148] yields polymers of probable structure



$R = CH_3—, C_2H_5—, (CH_3)_2CH—, (CH_3)_3C—$;
$R' =$ Alkylene, Arylene .

This view is based on analogy with the condensation of maleic anhydride with monosubstituted benzenes, in which cycloaddition takes place at the bond most remote from the substituent[149,150]. However, some results[151] indicate that the site of cycloaddition depends on the reaction temperature, and mixtures of isomers—or heterounit coplymers—may be obtained.

Table 1. Polyimides of general formula obtained by the polyaddition of bismaleimides to benzene[147].



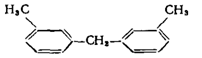
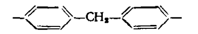
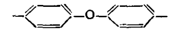
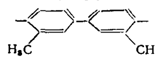
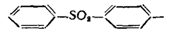
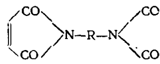
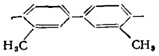
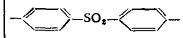
R	Yield, %	R	Yield, %
$—(CH_2)_2—$	95		80
$—(CH_2)_3—$	80		15
$—(CH_2)_6—$	70		30
	65		85

Table 2. Polyimides obtained by the photoaddition of alkylbenzenes to bismaleimides[146].



Alkylbenzene	R					
	$—(CH_2)_6—$					
	yield, %	t_{soft}*, °C	yield, %	t_{soft}*, °C	yield, %	t_{soft}*, °C
Benzene	70	410	65	485	85	450
Toluene	40	380	45	390	89	400
Ethylbenzene	23	390	0	—	50	350
Cumene	28	390	0	—	60	420
t-Butylbenzene	34	425	44	370	85	400

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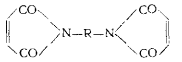
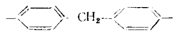
*t_{soft} = temperature at which softening begins.

Table 2 gives the yield and the thermal stability of polymers obtained after the optimum time of exposure, which varied from 5 to 40 h for different imides[148]. The yield decreases significantly on passing from benzene to alkylbenzenes. On the basis of the inductive effect the reactivity should increase in the sequence—methyl < ethyl < isopropyl < *t*-butyl—but the steric effect would diminish the reactivity in the same sequence. The net effect determines the polymer yield for different hydrocarbons. The terminal members of the sequence show the same net effect of the opposing factors, so that the yields are similar. The absence of a polymer in the reaction of ethylbenzene and cumene with 3,3′-dimethylbiphenylbismaleimide may be due to greater steric hindrance caused by the *o*-methyl groups. The higher yield with the bismaleimide containing a sulphonyl group is probably due to the fortunate combination of the electron-donating power of the alkyl groups with the strong electron-accepting influence of the sulphonyl group. All the polymers obtained are either only partly soluble or completely insoluble in organic solvents and trifluoroacetic acid.

Soluble polyimides or analogous structure can be obtained in high yields from the reaction of bismaleimides with several benzene derivatives in the presence of acetophenone in solution in excess of the aromatic hydrocarbon or in a mixture of the latter with chloroform or alcohol during ultraviolet irradiation for 18–20 h.[152-154] The yield and the viscosity of the resulting polymers depend significantly on the nature and the concentration of the monomers, the temperature, the duration of exposure, and other factors[154-156]. Table 3 shows that hexamethylene-*NN'*-bismaleimide is the most active among the bisdienophiles investigated. The reactivity of the bismaleimide decreases sharply when the aliphatic is replaced by an aromatic bridge. A possible reason is diminished conjugation of the carbonyl group with the double bond. The comparatively low viscosity of the polyimides is probably due to precipitation of the polymers because of poor solubility in the reaction medium and to cessation of chain growth at low degrees of polymerisation.

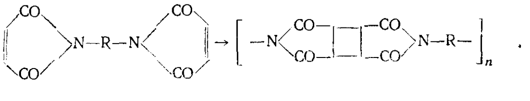
Table 3. Polyimides from aromatic derivatives and bismaleimides[152-154].



Aromatic diene	R							
	$-(CH_2)_2-$		$-(CH_2)_6-$		$-(CH_2)_{10}$			
	yield, %	η_{sp}, dl g^{-1}	yield, %	η_{sp}, dl g^{-1}	yield, %	η_{sp}, dl g^{-1}	yield, %	η_{sp}, dl g^{-1}
Benzene	73	0.13	56	0.44	30	0.14	7	0.06
Toluene	55	0.12	73	0.55	—	—	8	0.03
o-Xylene	51	0.09	71	0.14	—	—	18	0.11
m-Xylene	68	0.07	—	—	—	—	—	—
p-Xylene	—	—	61	0.30	—	—	—	—
Ethylbenzene	60	0.12	80	0.10	45	—	10	0.07
Cumene	45	0.10	67	0.09	15	0.20	5	0.09
Chlorobenzene	19	0.02	20	0.04	—	—	7	0.03
Diphenyl ether	35	0.02	40	0.03	—	—	—	—

Raising the temperature and lengthening the time of irradiation increase the yield of polymers, which reaches its maximum value more rapidly the higher the temperature. With certain pairs of monomers, however, prolonged exposure at high temperatures (40–80°C) leads to diminished yields, probably because of breakdown of the thermally unstable reaction complex formed initially. Higher yields of polymer are obtained with increase in the concentration of the bismaleimide in the reaction mixture. The yield increases on addition of an inert solvent (acetone, chloroform, alcohol), because of improved solubility of the bisimide and hence the possibility of reaction occurring in more concentrated solutions.

In mixtures of solvents, however, the main reaction is accompanied by secondary homopolymerisation of the bisimide:



This leads to the formation of mixed polymers with cyclobutane rings in the chain, as is confirmed by fractionation and by infrared and nuclear magnetic resonance spectroscopy of the polymers[156].

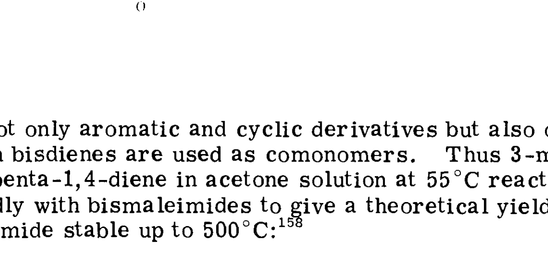
Mixed Diels–Alder polyimides have been obtained also by the copolymerisation of two aromatic dienes with bismaleimides[156,157]. The yield is 20–80%, and the intrinsic viscosity 0.01–0.15 dl g^{-1}. They are inferior to homopolyimides in thermal stability, and begin to decompose at 330–370°C. Increasing the content of substituted benzene segments in the chain in mixed polyimides based on benzene and alkylbenzenes produces a monotonic fall in viscosity.

An investigation of the influence of the composition of the initial mixture of aromatic hydrocarbons on the yield and the properties of the mixed polyimides has shown[157] that, according to their reactivity towards bismaleimides, they can be arranged in the sequence

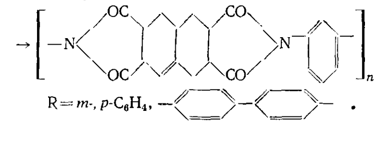
cumene ⩾ toluene > benzene ⩾ diphenyl ether > chlorobenzene.

It follows from this sequence, which coincides with that deduced from a study of homopolymerisation, that the rate of polymerisation increases when the aromatic hydrocarbon contains electron-donor substituents of small bulk, and decreases in the presence of electron-accepting substituents.

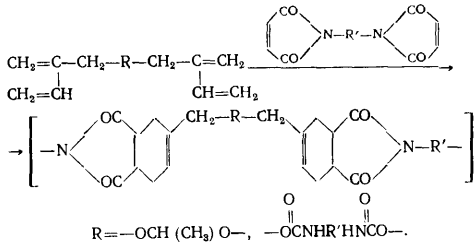
The above results show that under certain conditions many benzene derivatives are able to undergo Diels–Alder reactions with bismaleimides just as actively as cyclic dienes. Among other aromatic compounds only 9-anthraldehydebisazine and 1,5-di(anthr-9-yl)penta-1,4-dien-3-one have been mentioned[127] as developing the diene character of anthracene on reaction with bismaleimides:



Not only aromatic and cyclic derivatives but also open-chain bisdienes are used as comonomers. Thus 3-methylenepenta-1,4-diene in acetone solution at 55°C reacts rapidly with bismaleimides to give a theoretical yield of a polyimide stable up to 500°C:[158]

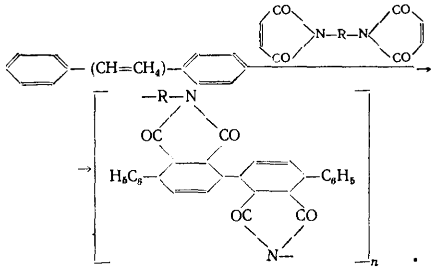


The same study used acetals and biscarbamates of 2-methylenebut-3-enol as bisbutadienes. Their polymerisation with phenylene-*m*- or *p*- or with biphenylylene-4,4′-bismaleimides in DMF solution at 100°C gave polyimides:

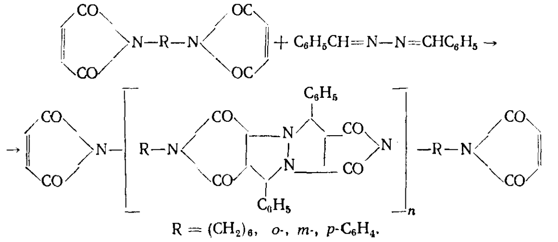


The yield for polymers varying in structure was 50–76%, with $[\eta] = 0.05–0.20$ dl g^{-1} and softening temperatures from 74 to 194°C.

Another example of an acyclic diene is 1,8-diphenyloctatetraene[125,126]. Polymers were obtained from it in theoretical yield, but the reduced viscosity was insignificant:



Benzylideneazine may act as a kind of acyclic diene in Diels–Alder reactions[159], adding at the 1,3-position to bismaleimides to form polyimides:



Polymerisation takes place in the melt at 180–190°C. The specific viscosity of the polymers is 0.13–0.30 dl g^{-1}, and their softening temperature 238–300°C.

Thus the Diels–Alder reaction ensures growth of the polymer chain to give linear polyimides when bisimides of unsaturated acids (mainly maleic) are treated with various dienes. The reaction takes place in solution or in the melt. The temperature and the duration of the synthesis are determined by the nature of the diene, the dienophile, and the solvent. In several cases active dienes react with bisimides under mild conditions, under which polymers of high molecular weight can be obtained. A peculiarity of this reaction is its reversibility, leading at high temperatures to formation of the initial components. Furthermore, the process is sometimes complicated by secondary 1 + 2 cycloaddition, causing cross-linking of the polymer chains.

Among the advantages of this reaction is that polyimides can be obtained with 100% imidisation. In most cases volatile reaction products are absent. These factors enable dense and non-porous polymers of high thermal stability to be obtained, which are promising for practical utilisation.

The above Review of published information shows that cyclic imides of di- and tetra-carboxylic acids are highly active monomers, and can be used in polycondensation, migration polymerisation, and cycloaddition reactions. The resulting open-chain or cyclic polymers possess several interesting properties.

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Quantitative "Chemical Structure-Biological Activity" Relations

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The principal methods used to obtain quantitative relations between chemical structure and biological activity are reviewed and the postulates, possibilities, and prospects of these methods are examined.
The bibliography includes 299 references.

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I. INTRODUCTION

The determination of the relations between the chemical structures of substances and their pharmacological activities is the most important task in the synthesis of highly effective and selective medicinal drugs. Biochemical pharmacology is as yet incapable of formulating rigorously the problems of specific synthesis. Nevertheless, an enormous scientific effort and capital investment are being devoted to the development of new drugs[1]. In this situation one is justified in attempting to compile empirical and semiempirical rules linking individual characteristics of the structures of substances and their effect on biological systems.

Extensive experimental data have now accumulated showing that there are definite relations between the physicochemical properties of a substance and its biological activity. The elucidation of the origin of the empirical relations between the properties of compounds *in vitro* and their biological action on the organism should make it possible to arrive at ideas concerning the mechanisms of biologically important chemical reactions and to establish on this basis well-founded recommendations for chemists working in the field of synthesis and, on the other hand, to predict the possible specificity and effectiveness of the biological action of newly synthesised substances, shortening thereby the laborious and expensive stages involving biological tests.

The possibility of determining structure-activity relations arose approximately one hundred years ago when it was observed[2] that the intensity of the narcotic action of certain substances decreases with increase of their solubility in water. A little later a relation was noted between narcotic activity and the distribution of substances in a water-lipid system[3,4]. A whole series of physicochemical parameters of substances, whose relation with narcotic activity and toxicity has been elegantly described by Lazarev[5,6], was established subsequently.

Despite the limited and qualitative nature of the majority of structure-activity relations observed in the first half of the XXth century, the justification of the hypothesis that the biological activity of a substance can be accounted for in individual instances by *in vitro* studies and described on the basis of the laws of physical chemistry and in terms of its concepts must be regarded as the general outcome of such relations.

Modern approaches to the structure-activity problem (based largely on the principles of physical and theoretical chemistry) are examined below. With their aid one may now hope to restrict the number of total syntheses and the biological screening of all substances which seem to be promising as medicinal drugs on the basis of general considerations.

The assertion that the structure of a substance and the biological response caused by it are involved in an unambiguous cause and effect relation, which is usually readily accepted on trust, must in fact be regarded as only one of the postulates underlying the approach to the structure-activity problem[7,8]. The most general postulates of this type may be reduced to the following.

1. The structure S of a chemical compound Y, designated by S_y, can be expressed in terms of a set of structural parameters $S_y = \{S_y^i\}$, where $i = 1, 2, \ldots, n$.

2. There is a relation between the structure of a substance and its biological activity, i.e. there is a function $F_y(S_y, A_y)$ relating the activity A of the substance Y to its individual characteristics—$F_y(S_y^i, A_y)$.

3. If the form of the function $F(S, A)$ has been established, the function may be extrapolated to compounds of the series Y_1, Y_2, Y_3,... with similar structures, differing to the substituents X_1, X_2,..., or by their positions in the molecule.

4. The sequence of the activities of a series of compounds, for example, $A_{X_1} > A_{X_2} > A_{X_3}$ may be deduced by analysing the set of functions $F_{Y_1}(F_{Y_1}, A_{Y_1})$, $F_{Y_2}(S_{Y_2}, A_{Y_2})$,... .

The prediction of biological activity is restricted to a series of compounds related by common structural features, it being implied that a "leading" structure has already been established and that the application of a particular approach should reduce the number of experimental tests on the biological activities of the members of the series.

In order to obtain a working model [i.e. $F(S, A)$], the reliability of which is to be subsequently estimated, it is suggested that the molecules of a biologically active substance undergo a series of physicochemical and chemical transformations in the organism: dissolution, sorption, partition, binding, chemical reactions, segregation, etc. Evidently, any of these stages or their combination may determine in each specific instance the specificity of the pharmacological action of the substance or may constitute the rate-limiting stage in the overall effect, determined as biological activity.

If the first condition holds, i.e. the physicochemical characteristics of the substance reflect its structure by a set of some of its parameters, then, in order to determine the form of $F_Y(S_Y, A_Y)$, it is necessary to obtain A in a quantitative form, namely $[A]$†. The quantity $[A]$, usually determined by means of biological tests, is, firstly, a statistical mean quantity and, secondly, it can reflect only the final results of the effect of the substance on the organism or the system simulating it. In fact the final result may be a consequence of one or several stages of the action of the substance. Hence it is clear that the most complex task in the determination of $F_Y(S_Y, A_Y)$ is the parametrisation of $[A]$.

If the observed biological response BR to the organism or the system simulating it to a certain substance is a consequence of a sequence of physicochemical processes involving the substance, then the time t elapsed between the onset of the action of the substance and its final result may be related to a stage controlling the rate of the process. If the substance at an initial concentration C_0, giving rise to a standard biological response, is introduced into the biological system, there is a probability N that an amount of the substance C_0N will reach sites with which it reacts and this leads to [BR]† after a period Δt. In this case the rate of the process can be represented in the following form (for a detailed treatment, see Section IV)[8,11,12]:

$$\frac{d[BR]}{dt} = KC_0N\bar{k}_i, \qquad (1)$$

where K is a proportionality coefficient relating the rate of the biological response[11,12] to the rate of the controlling stage, while $\bar{k}_i$ is the rate constant or equilibrium constant for this stage.

The above considerations and Eqn. (1) have not been rigorously proved. The point is that the standard biological response (ED_{50}, LD_{50}, etc.) does not contain in an explicit form information about the rate d[BR]/dt. Furthermore, in a real case the rate constant for the process $\bar{k}_i$ may be determined by any individual stage, a multiple repetition of such stages, or their combination. Function (1) should therefore be regarded merely as formally reflecting the relation between [BR] and a hypothetical rate-determining steady-state physical or chemical process. However, by introducing the additional postulate

$$\frac{d[BR]}{dt} = \text{const}, \text{ i.e. } KC_0N\bar{k}_i = \text{const}, \qquad (2)$$

it is possible to obtain a set of functions $F_Y(S_Y^i, A_Y)$ analogous to the experimentally observed set[9-11] (for further details, see Section IV), taking into account the fact that $1/C_0$ is usually employed as $[A]$.

The choice of $1/C_0$ as a measure of the effectiveness of the biological action of the substance $[A]$ cannot at present be rigorously justified. Nevertheless, the legitimacy of employing $1/C_0$ as a measure of A follows to some extent from experimental data[13-16] and a model of the equilibrium distribution[17]. Indeed if the chemical potentials of the substance at the site of its administration and at the site of its action are the same[17], its initial concentration (C_0) must determine its concentration in a specific region of the biophase (C_B), binding to which (i.e. reaction with this region) gives rise to the biological effect, since in this case the law of the partition of the substance between the phases C_B/C_0 = const. holds, whence the validity of $1/C_0$ as a criterion of the effectiveness of the biological action is evident. On the other hand, if the biological action of the substance is determined by the inhibition of a specific enzyme of the biophase, its inhibition rate constant may be used to estimate $[A]$ (O'Brien[13]); experimental evidence for the relation between $1/C_0$ and the inhibition rate constant has been obtained[15,16,18].

The theoretical case where the time of attainment of a definite state of inhibition of the enzyme is inversely proportional to C_0 is obtained for second-order reactions. Indeed, in this case $[A] = K_{0.5}^i = k_1(1/C_0)$ to within the constant k_1. In fact postulate (2) or its logarithmic form

$$\lg[A] = \lg(1/C_0) = \text{const} + \lg N + \lg K + \lg \bar{k}_i \qquad (3)$$

imply merely that, for the same rate of the rate-limiting stage, all the substances in the series, i.e. related compounds, should give rise to an identical biological response over a fixed time interval regardless of their structure and composition. Because of this, the quantity $-dC_{cr}/dt$, in the form $-dC_{cr}/dt = \bar{k}_iNC_0$, should be introduced directly into Eqn. (1) and not the formal quantity d[BR]/dt. In this form the problem is stated correctly and reduces to the determination of the dependence of $\lg(1/C_0)$ on various physicochemical parameters.

In order to facilitate the mathematical interpretation of Eqn. (3), it is assumed that the reaction limiting the rate of the process at a given stage is of first (or pseudofirst) order. This is possible if (1) only a small proportion of the reacting active centres in the organism interact with the test substance and (2) the substance is present in the organism in a considerable excess relative to the number of reactive sites. The second instance is frequently obtained under *in vitro* conditions, i.e. in a model physicochemical system, while the first probably obtains under the real conditions occurring when an organism is acted upon by the given substances.

The origin of the structure–activity relations is deduced by comparing the results of independent physicochemical and biological studies on the relevant substances. Table 1 presents the forms of biological action for which a correlation between the type of biological action of the substance and its physicochemical characteristics has been established empirically.

If it is assumed that Eqn. (3) is correct, then, for a quantitative expression of the influence of substituents on $\lg\bar{k}_i$ and hence on $\lg[A]$, it is necessary to take into account, to a first approximation, the hydrophobic, electronic, and steric components of the interaction, which may be represented in the form of their linear combination:

$$\lg\bar{k}_i = f_h(S_h) + f_e(S_e) + f_s(S_s). \qquad (4)$$

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†Here and henceforth $[A]$ and [BR] are a quantitative measure of the activity, expressed in terms of the concentration, and a quantitative measure of the biological effect, expressed in terms of arbitrary units, respectively.

On combining Eqns. (3) and (4), we obtain

$$\lg [A] = \lg (1/C_0) = f_h(S_h) + f_e(S_e) + f_s(S_s) + \lg N + \text{const.} \qquad (5)$$

The specific form and significance of each term of Eqn.(5) can be found in different ways as a function of the model adopted or the available experimental observations (see below).

Table 1. The forms of biological action for which a quantitative correlation has been established with the physicochemical parameters of substances and the parameters of their model interactions.

Physicochemical characteristics of substance	Type of biological action	References	Sources of tabulated values of physicochemical parameters
Logarithm of partition coefficient $\lg P$	Bacteriostatic activity	77,84,87, 147-149	
	Narcotic activity	12,135,150, 151	41,176-178
	Inhibition of enzymes	12,18,77, 152,153	
	Protein binding	12,53,135, 154-156	
	Anticonvulsant activity	77,157	
	Local anaesthetic activity	77,151	
	Permeability of tissues or artificial membranes	12,158,159	
	Spasmolytic activity	77,135	
	Carcinogenic activity	160	
	Inhibition of absorption of oxygen	135	
	Localisation of boron in brain	12,161	
	Toxicity to multicellular organisms	162	
	Inhibition of cell division	135	
	Androgenic activity	163	
	Anabolic activity	163	
	Antitumour activity	164	
	Inhibition of luminescence	135	
	Action on central nervous system	165-167	
	Antagonism to histamine, serotonin, etc.	135	
	Fibrinolytic activity	156,168	
	Inhibition of Hill reaction	169-171	
	Analgesic activity	150	
	Anti-inflammatory activity	172	
	Growth-activating activity	173	
	Anti-electric shock activity	174	
	Antifungal activity	175	
Lipophilic parameter π	Bacteriostatic activity	77,81,147 179-182	41,52,72, 177, 178 210,211
	Narcotic activity	12,60	
	Inhibition of enzymes	18,86,179, 183-191	
	Protein binding	53,156,192	
	Antimalarial activity	193	
	Insecticidal activity	194	
	Local anaesthetic activity	195	
	Antihelminthic activity	88	
	Sweetness (relative)	196	
	Hypotensive activity	197	
	Localisation of boron in brain	12	
	Synergistic activity	11,76	
	Inhibition of Hill reaction	198	
	Natrivretic activity	91	
	Haemolysis of erythrocytes	128,148	
	Adrenergic blocking activity	199,200	
	Antiarrhythmic activity	94	
	Action on potential of axon	128	
	Inhibition of complement	201	
	Progesterone etc. activity	144,202	
	Antifungal activity	203	
	Phytotoxic activity	81,179	
	Inhibition of cell division	204	
	Antiphagocytic activity	205	
	Toxicity to multicellular organisms	179	
	Acaricidal activity	206	
	Antogonism to histamine, serotonine, etc.	207	
	Inhibition of saliva secretion	179	
	Fungicidal activity	98	
	Herbicidal activity	68,208	
	Anti-inflammatory activity	179	
	Depolarising action on electrically excited membranes	179	
	Inhibition of mitochondrial electron transport	209	
Thin-layer chromatographic (t.l.c.) parameters R_M and ΔR_M	Bacteriostatic activity	57,182,212	57,178,212, 216,217
	Toxicity to multicellular organisms	55,212	
	Protein binding	96,178,212	
	Androgenic activity	163	
	Synergestic activity	163	
	Haemolysis of erythrocytes	148,178,212	
	Hypoglycaemic activity	96	
	Anabolic activity	163,212	
	Inhibition of mitochondrial electron transport	209,212,213	
	Progesterone etc. activity	214	
	Inhibition of Hill reaction	179	
	Analgesic activity	212	
	Fungicidal activity	212	
	Herbicidal activity	212	
$\delta_{t.c.}$	Inhibition of Hill reaction	179,215	215
Parachor Pr, $g^{1/4}\,cm^3\,s^{1/2}\,mole^{-1}$	Bacteriostatic activity	42,60,62	43,60,61 220-222
	Narcotic activity	42,60,61, 218	
	Protein binding	60	
	Inhibition of embryonic development	60	
	Inhibition of cell division	42	
	Thyromimetic activity	62	
	Local anaesthetic activity	62	
	Fibrinolytic activity	62	
	Haemolysis of erythrocytes	62	
	Action on potential of axon	62	
	Sympatheticomimitic activity	62	
	Parasympatheticolytic activity	62	
	Anti-inflammatory activity	219	
Molar volume V_M, $cm^3\,mole^{-1}$	Bacteriostatic activity	42,70	44
	Narcotic activity	42,61,70	
Molecular connectivity χ_M	Narcotic activity	67	67
	Enzyme inhibition	67	
	Antifungal activity	67	
Molecular weight M, $g\,mole^{-1}$	Narcotic activity	60,61	223
	Protein binding	60	
	Inhibition of embryonic development	60	
Logarithm of solubility in water $\lg C_s$ ($mole\,litre^{-1}$)	Bacteriostatic activity	42	224,225,300
	Narcotic activity	42	
Partial pressure (in model system) p, mmHg	Anaesthetic activity	179,26	
Hildebrand's solubility parameter δ, $cal^{1/2}\,cm^{3/2}$	Haemolysis of erythrocytes	227	65,228,229
Molar attraction constant Fa, $cal^{1/2}\,cm^{3/2}\,mole^{-1}$	Narcotic activity	60,61,66	60,66
	Inhibition of embryonic development	60	
Van der Waals' constant a, $litre^2\,atm\,mole^{-2}$	Narcotic activity	142	230
Hammett's constant σ (σ_M, σ_π)	Bacteriostatic activity	12,147,180 181	69,72,210 233-236
	Enzyme inhibition	12,18,77 184-188, 231,232	
	Haemolysis of erythrocytes	12	
	Local anaesthetic activity	195,237	
	Antagonism to histamine, serotonin, etc.	238	
	Sweetness (relative)	196	
	Inhibition of mitochondrial electron transport	209	
	Toxicity to multicellular organisms	162,179	
	Andrenergic blocking activity	199,200	
	Inhibition of hormonal activity	239	
	Fibrinolytic activity	156	
	Hypotensive activity	197	
	Antimalarial activity	193	
	Antiphagocytic activity	205	
	Acaricidal activity	206	
	Growth activating action	173	
	Antielectric shock activity	174	
	Antifungal activity	175	
	Herbicidal activity	68,208	
Inductive and resonance components σ_I and σ_R of Hammett's constant	Enzyme inhibition	18,129,185, 240	235,241
	Antagonism to histamine, serotonin, etc.	238	
	Antiviral activity	242	
Electron donor and electron acceptor substituent constants σ^+, σ^-, $\Delta\sigma_R^+$	Enzyme inhibition	12,18,77 129,179	69,90,235 241,243-24
	Haemolysis of erythrocytes	12	
	Inhibition of complement	201	
	Toxicity to multicellular organisms	12	

Table 1. (cont'd).

Physicochemical characteristics of substance	Type of biological action	References	Sources of tabulated values of physicochemical parameters
Taft's inductive constant σ^*	Bacteriostatic activity	87,149	235,245,246
	Enzyme inhibition	18,195,240	
	Anticonvulsant activity	157	
	Adrenergic blocking activity	127	
	Action on central nervous system	167	
	Inhibition of saliva secretion	179	
	Antielectric shock activity	174	
	Depolarising action on excited membranes	179	
	Antifungal activity	175	
Radical substituent constants $\sigma^{\cdot}$ and E_R	Bacteriostatic activity	77,148	74,76
	Enzyme inhibition	18,77	
	Local anaesthetic activity	77	
	Synergistic activity	12,76	
Swain and Lupton's parameters and $\mathcal{R}$	Antagonism to histamine, serotonin, etc.	238	69,72,210
	Enzyme inhibition	18,185	
	Progesterone activity	202	
Charge transfer constant C_T	Enzyme inhibition	18,78	78
	Carcinogenic activity	79,80	
Change in ionisation constant ΔpK_a	Bacteriostatic activity	81,79,181, 182	247,248,284
	Enzyme inhibition	12,13,18,77, 179-185,191	
	Inhibition of oxygen adsorption	135	
	Inhibition of cell division	135	
	Inhibition of mitochondrial electron electron transport	209	
	Anti-inflammatory activity	179	
	Natriuretic activity	91	
	Phytotoxic activity	81	
Molar electronic polarisation P_E, cm^3 mole^{-1}	Bacteriostatic activity	85,87	
	Enzyme inhibition	18,86,185	
	Anaesthetic activity	249	
Polarisability α, cm^3	Local anaesthetic activity	83	60,83
Molecular refraction MR, cm^3 mole^{-1}	Enzyme inhibition	18,153,188 232	72,210,222, 251,252
	Inhibition of complement	201	
	Narcotic activity	61	
	Progesterone activity	202,250	
Dipole moment μ, D	Antihelminthic activity	88	253
	Enzyme inhibition	18,152	
Ionisation potential I, eV mole^{-1}	Narcotic activity	254,255	83,257,258
	Local anaesthetic activity	83	
	Carcinogenic activity	79,256	
Polarographic half-wave potential $\varphi_{1/2}$, V	Bacteriostatic activity	84	230
Taft's steric parameter E_s	Bacteriostatic activity	37,149	128,235
	Enzyme inhibition	18,129,185, 186,188, 190,240	
	Anticonvulsant activity	157	
	Antagonism to histamine, serotonin, etc.	102	
	Antiviral activity	8	
	Synergistic activity	11,76	
	Motor activity	259	
	Fibrinolytic activity	156,168	
	Antiphagocytic activity	205	
	Antielectric shock activity	174	
	Antiallergic activity	97	
	Antifungal activity	175	
Corrected Taft's steric parameter E_s^c	Enzyme inhibition	195	235
	Adrenergic blocking activity	127	
	Depolarising action on excited membranes	179	
Van der Waals' radius r_V, Å	Bacteriostatic activity	37	260
	Adrenergic blocking activity	200	
Surface tension γ, dyn cm^{-1}	Narcotic activity	261,262	221,265,266
	Action on central nervous system	263	
	Local anaesthetic activity	264	
Surface pressure π_s, dyn cm^{-1}	Action on central nervous system	226,263,257	265
	Local anaesthetic activity	237	
Hydrophilic-lipophilic balance HLB	Modification of herbicidal activity	68	268
Molar heat of adsorption Q_{ads}, cal mole^{-1}	Permeability of tissues and artificial membranes	269	269
	Inhibition of oxygen absorption	269	
	Inhibition of luminescence	269	
Logarithm of specific rate of dissolution lg K_{diss}, μmole cm^{-2} s^{-1}	Local anaesthetic activity	59	
Constant for binding by a model receptor (protein, etc.) K_b	Analgesic activity	145	41
	Antitumour activity	270	
	Carcinogenic activity	271,272	
Molar diamagnetic susceptibility χ, cm^3 mole^{-1}	Narcotic activity	61	202

Table 1. (cont'd).

Physicochemical characteristics of substance	Type of biological action	References	Source of tabulated values of physicochemical parameters
Chemical shift of atoms X in NMR spectrum δ^X, p.p.m.	Hypoglycaemic activity	90,96	274-279
	Natriuretic activity	91	
	Fungicidal activity	98	
Spectroscopic data: vibration frequency ν, s^{-1} wavenumber ω, cm^{-1}	Bacteriostatic activity	95	
	Antiarrhythmic activity	94	
	Antiallergic activity	97	
Peripheral parameter characteristing the properties of substituents in steroids c	Progesterone, etc. activity	144	250
Principal quantum-chemical parameters overall charge of π-electrons at r atom q_r or ϵ,C	Bacteriostatic activity	120	
	Enzyme inhibition	18,109,232 114,120,	
overall $(\sigma + \pi)$ charge of electrons at r atom Q_r^T, C	Bacteriostatic activity	280	
	Anticholinergic activity	113	
	Enzyme inhibition	18,110,152	
Energies of highest occupied and lowest unoccupied molecular orbitals E_{HOMO} and E_{LUMO}, eV	Bacteriostatic activity	280	
	Local anaesthetic activity	83	
	Analgesic activity	281	
	Hypotensive activity	115	
	Action on central nervous system	282,283	
	Inhibition of cell division	204	
Electrophilic (E) and nucleophilic (N) capacities for ultradelocalisation S_r^E and S_r^N	Bacteriostatic activity	114,120	
	Anticholinergic activity	113	
	Hypotensive activity	115	
	Nicotine-like activity	12	
Free valence index F_r	Bacteriostatic activity	114	
Atomic-orbital coefficient of r atom C_r	Bacteriostatic activity	120	

We shall adopt the convention that all the approaches to the structure–activity problem, including the examination [in terms of Eqn. (3)] of specific physicochemical characteristics of the given substance, are semiempirical.

The contribution of the second group of methods (empirical methods) consists in a systematic analysis of studies of biological activity in order to discover the structural elements and their combinations characteristic of a particular type of activity. We have included in the same group methods for the estimation of the mathematical contribution of definite structural elements to the biological activity of the compound.

II. THE METHOD OF SUBSTRUCTURAL ANALYSIS. THE PATTERN RECOGNITION METHOD

Both these methods are based on the hypothesis that the biological activity of a substance is due to the presence in its molecule of definite structural elements (substructures).

The frequency of the activity of the substructure L characterises the contribution which the substructure makes to the probability that the compound is biologically active[19]. It is expressed numerically as the ratio of the number of biologically active substances containing a definite structural unit (B) to the total number of compounds analysed where this substructure is also encountered (T), i.e. $L = B/T$.

Using a descriptive system of fragment coding[20,21], capable of distinguishing 1200 structural fragments—functional groups, chains, rings, etc.—and 110 types of their combinations, a formalism[22] and a computer program were developed; the latter was capable of determining L for compounds differing appreciably in their chemical structure and exhibiting a known type of biological activity, which were compared with the same values for compounds analysed for potential biological activity.

The attempt[19] to estimate the antiarthritic-immunoregulatory activity of 850 preparations of different structures and with different mechanisms of their pharmacological activity in terms of the criterion L, regardless of tests based on physiological methods[23], led to the following findings:

(1) simple identification of the structural fragments characteristic of the most active substances of this group does not permit the choice, as was to be expected, of the optimum compounds and hence the determination of the sequence based on their increasing or decreasing activities;

(2) the experimental frequency tables for the activities of substructures, including the values of L for 492 structural fragments encountered in the most active compounds with a given type of activity, made it possible to establish a series of compounds based on decreasing activities and consistent with the experimental series‡.

Next the same program was used to search for substances with antiarthritic-immunoregulatory activity among 703 substances which had not yet been tested. It was shown[19] that the criterion L is suitable not only for the determination of the potential activities of a wide variety of types of compounds but also for the recommendation of the required combination of substructures in the synthesis of compounds previously unknown as antiarthritic-immunoregulatory agents.

Naturally in the form in which it has been proposed the criterion L cannot be referred directly to structure-active relations. When the pattern recognition method is applied[24,25], apart from the substructural principle of characterising substances their physicochemical parameters are introduced as well. In this case, a series of preselected chemical compounds with a definite specificity of their biological action (learning series including more than 100 substances) is represented by a surface in n-dimensional space, where the coordinates are formal equivalents of the structural fragment and the physicochemical parameters of the substance; the points on the surface correspond to individual compounds. The test substance or group of substances is treated formally in terms of the same features as the learning series after which one finds how close they are located in the given n-dimensional space to the points corresponding to the active compounds in the learning series. A special method[25] makes it possible to formulate individual groups of features in terms of space vectors, which makes it possible to reduce the number of variables and to discover fragments characteristic of active compounds. According to Chu et al.[24], the combined use of fragment and physicochemical criteria to characterise substances permitted the prediction with 80–90% probability of antitumour activity in a series of 17 previously uninvestigated compounds.

III. THE MATHEMATICAL ADDITIVE MODEL

The mathematical additive model (MAD)[26] is based on the hypothesis of the independent additive contribution of substituents to $[A]$ for a number of compounds Y_1, Y_2, Y_3,..., differing by the substituents X_1, X_2, X_3,..., the mathematical contribution of the molecular skeleton being assumed to be constant. Accordingly one can write

$$[A] = \sum_i a_i x_j + \lambda, \tag{6}$$

where a_i is the mathematical expression for the contribution of the ith substituent to $[A]$, $x_j = 0$ or 1 depending on the absence or presence of the ith substituent, and λ is the constant mathematical contribution of the skeleton to $[A]$.

The MAD imposes an additional limitation on the overall contribution of substituents to biological activity for the same position in the entire series of compounds. For example, if three substituents A, B, and C may exist in the same structural element, then

$$\sum_i^k a_i(\mathrm{A}) + \sum_i^l a_i(\mathrm{B}) + \sum_i^q a_i(\mathrm{C}) = k a_i(\mathrm{A}) + l a_i(\mathrm{B}) + q a_i(\mathrm{C}) = 0, \tag{7}$$

where k, l, and q are the numbers of compounds containing the substituents A, B, and C respectively in the given position. The contribution of any substituent can therefore be expressed in terms of a linear combination of the contributions of the remaining substituents. Evidently, if the series of compounds tested contains h structural elements, in which there may be m substituents, then the solution of the system of equations thus formulated requires n equations with $m - h$ independent variables. The individual contributions of the substituents can be used to calculate $[A]$ for compounds of the series which have not yet been investigated.

The scope of the MAD has been frequently analysed[27-32] and attempts have been made to improve the model[33,34]. Using the same hypothesis of additivity, Eqn. (6) can be written in the form

$$\lg \frac{[A_1]}{[A_0]} = \sum_i G_i x_j, \tag{8}$$

where the subscripts 0 and 1 refer to $[A]$ for the unsubstituted and substituted compounds, G_i is the logarithm of the change in $[A]$ when the ith substituent is introduced instead of $X_1 = H$, and x_j has the same significance as in Eqn. (6). For a homologous series, $\lg[A_0] = \text{const.}$ and Eqn. (8) becomes

$$\lg [A_1] = \sum_i G_i x_j + \text{const.} \tag{9}$$

This stage already simplifies the MAD greatly: firstly, the constant term proves to be the activity of the initial unsubstituted compound and not a derivative of the molecular skeleton; secondly, since $[A]$ in the modified model is considered in relation to the activity of a hydrogen-containing compound, one may disregard the restrictive relation (7), which reduces the number of equations.

Despite the artificiality of the hypotheses underlying the MAD (the additivity and independence of the contributions of the substituents), the agreement between the experimental and calculated values of $[A]$ may be satisfactory, provided that (a) successive structural changes in series of compounds are investigated and (b) the results of biological tests used for the determination of the relative contributions of substituents are sufficiently accurate[27].

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‡In order to avoid "discoveries" compounds constituting the basis of the compilation of the Tables, these compounds were excluded from the total number of substances tested.

The fundamental effectiveness of the MAD may be demonstrated. We shall assume that it is necessary to test a series of compounds where the substituents may be located in four positions ($h = 4$) and the number of substituents in the compound is varied: $m = 2, 3, 4$, or 5. The theoretically possible number of variants of molecules is then 120. The number of structural elements which must be introduced into the MAD is $\Pi = \sum^{h} m_i + 1 = 15$, where unity represents the contribution of the molecular skeleton. Consequently, in order to determine theoretically the values of $[A]$ for 120 compounds, it is sufficient to carry out only 11 tests of their biological activity (i.e. $\Pi - h$ tests). In view of the low accuracy of biological experiments, in order to obtain a reliable result in practice, it is desirable to have the largest possible number of experimental data[28].

Allowance for the mutual influences of the substituents in the MAD constitutes a more realistic approach[31,32]. For this purpose, the terms G_i^*, taking into account the change in $[A]$ owing to the interactions of the substituents, are introduced into Eqn. (9):

$$\lg [A] = \sum_i G_i x_j + \sum_i G_i^{\bullet} x_i x_j \ldots + \text{const.} \tag{10}$$

For example, if the compound contains the substituents X_1, X_2, and X_3, then, when account is taken of their mutual influence, we have $\lg [A] = G_1 x_1 + G_2 x_2 + G_3 x_3 + G_1^* x_1 x_2 x_3 + G_2^* x_1 x_2 + G_3^* x_1 x_3 + G_4^* x_2 x_3 + \text{const.}$ It has been shown[34,35] that the use of this procedure makes it possible to take into account the influence of the relative positions of the substituents on biological activity. Naturally, in this case there is a sharp increase of the number of terms in the equation and hence of the number of necessary biological tests, which reduces the practical scope of the application of the mathematical model.

Attempts have been described to relate the mathematical additive model to the mechanism of the action of substances[34,36-40].

The results accumulated hitherto concerning the application of empirical methods for the estimation of $[A]$ show that fairly similar values of $[A]$ may be obtained by independent computational and experimental methods. The practical use of the above methods requires a generalisation, systematic arrangement and representation in a form suitable for computer calculations of the extensive experimental data from studies on the biological activity of chemical compounds, and the development of a single system for the mathematical representation of the structures of substances.

IV. THE MULTIPARAMETER REGRESSION METHOD

The qualitative relations established between the biological activity and physicochemical properties of substances[2-4] stimulated studies designed to discover the essential features of these relations. The first attempt of this kind involves the equilibrium distribution model (EDM).[17] It is based on the hypothesis that, after the introduction of the substance into a biological system, chemical equilibrium, determined by the equality of the chemical potentials (μ) of the substance in different phases, is established between its concentration at the site of administration and the concentration in the vicinity of the site of response. The constancy of the isonarcotic concentrations in the lipid phase C_{lip} followed from the results of tests on the narcotic activity of a wide variety of compounds[17]. At low concentrations $\mu = \mu_0 + RT \ln C$; hence, setting the values of μ for the lipid and aqueous phases equal and assuming that C_{lip} is constant, it is possible to obtain a relation between $\lg (1/C_0)$ and the partition coefficient of the substance in the biological system (P_{b}). The latter is as a rule unknown, but it has been established[17,41,42] that P for a model system (for example olive oil-water and octanol-water systems) may be used instead:

$$\lg (1/C) = a \lg P + b. \tag{11}$$

In Eqn. (11) $\lg P$ may be replaced by other physicochemical parameters of the substance, such as, for example, the parachlor (Pr), the molar volume (V_{M}), and the solubility ($\lg C_{\text{S}}$). The most complete information about structure-activity correlations based on the EDM has been published by McGowan[42]. On the basis of the theory of solubility, it is shown[42] that $\lg P$ can be represented by $\lg P = k_1 Pr + E_{\text{A}}$. On the other hand, the parachor may be related to $\lg C_{\text{S}}$ and V_{M} with the aid of the approximate relations $\lg C_{\text{S}} \simeq \lg C_l + k_2 Pr$ and $Pr \simeq k_3 V_{\text{M}}$, where E_{A} is a term taking into account the association of substances or their capacity for the formation of a hydrogen bond, C_l is the molar concentration of the substance recalculated for the pure liquid phase, and k are the corresponding proportionality coefficients. The relation between $\lg P$, on the one hand, and Pr, V_{M}, and $\lg C_{\text{S}}$, on the other hand, in the given model can be accounted for in terms of thermodynamic considerations, since the main contribution to $\lg P$ comes from the change in the entropy of the system owing to the rearrangement of the solvation shells of the molecules on passing from the aqueous to the organic phase. The degree of dehydration depends on a number of factors, in the first place on the size and polarity of the molecules of the substance and their packing density. $\lg C_{\text{S}}$, Pr, and V_{M} may be used as characteristics of these factors.

The possibility of using the additivity rules to predict the biological activity of substances on the basis of the additivity of the values of Pr and V_{M} was demonstrated for the first time with the aid of the equilibrium distribution model[42-44]. The limitations of the EDM are evident, since it takes no account of either the kinetics of the attainment of equilibrium in the system or of the mechanism of the chemical reactions occurring in it.

At the beginning of the 1960s Hansch and coworkers proposed an approach fundamentally different from the EDM. They suggested that the overall physicochemical process causing the biological response be regarded as a steady-state and not an equilibrium process[9]. They began with the assumption that the time interval corresponding to the biological test is insufficient for the attainment of chemical equilibrium. Hansch and Fujita[9] used the familiar scheme[45] for the biological activity of the substance:

$$\begin{array}{l} \text{Compound in extra cellular phase} \xrightarrow[\text{stage I}]{} \text{Site of action in cellular phase} \xrightarrow[\substack{\text{stage II} \\ \text{(rate-determining)}}]{\bar{k}_{\text{II}}} \\ \cdots \xrightarrow[\text{stage III}]{} \cdots \xrightarrow[\text{stage } n]{} \text{Biological response}. \end{array} \tag{12}$$

It was found that the principal stages at I and II—the migration of molecules from the very dilute solution outside the cell to a definite site within the cell and the chemical or physical process determining the overall rate of the biological response respectively. It was postulated that other stages (III...n) do not affect the observed biological response.

In order to derive a formula relating $\lg(1/C_0)$ to physicochemical parameters, Hansch and Fujita[9] used a phenomenological approach (see Section I). It follows from Eqn. (2), which can be rewritten in the form

$$\lg(1/C_0) = \lg N + \lg \bar{k}_{\text{II}} + \text{const} \qquad (13)$$

for scheme (12), that the problem reduces to expressing $\lg(1/C_0)$ in terms of the physicochemical parameters determining the values of $\lg N$ and $\lg \bar{k}_{\text{II}}$. On the basis of the relation observed by Collander[46,47] between $\lg P$ and the rate of migration of organic compounds through tissues and the nearly parabolic relation between $\lg(1/C_0)$ and $\lg P$ observed in a number of instances[9,12,48], it was assumed that N obeys the normal distribution law with respect to $\lg P$:

$$N = N_0 \cdot \exp\left[-\frac{(\lg P - \lg P_{\text{op}})^2}{b}\right], \qquad (14)$$

where P_{op} is the optimum value of P corresponding to the maximum value of $N = N_0$ and b is a constant. Hammett's equation

$$\lg \bar{k}_x = \rho\sigma + \lg \bar{k}_0, \qquad (15)$$

in which $\bar{k}_X$ and $\bar{k}_0$ represent the rate or equilibrium constants for *meta*- or *para*-substituted and unsubstituted benzene derivatives respectively (for the same reaction and under identical conditions), ρ is a constant for the given reaction, and σ the Hammett constant for the substituent, was used for the first time for the term $\lg \bar{k}_X$. After substituting Eqns. (14) and (15) in Eqn. (13), we obtain

$$\lg(1/C_0) = a_1(\lg P)^2 + a_2 \lg P + a_3\sigma + a_4, \qquad (16)$$

where a_1–a_4 are constants.

Eqn. (15) is a consequence of the application of the principle of linear free energy relations (PLE).[49–51] It can be used to express the rate or equilibrium constants ($\lg \bar{k}_X$) for a series of related compounds involved in similar reactions. One then obtains for different types of interactions equations which are analogous in form to Eqn. (15). Expressing $\lg \bar{k}_X$ in Eqn. (13) with their aid, it is possible to obtain a wide variety of equations taking into account the resonance, conformational, steric, and other factors influencing $\bar{k}_X$; in particular, the following expression has been obtained[11]:

$$\lg(1/C_0) = -a_1(\lg P)^2 + a_2 \lg P + a_3\sigma + a_4E_s + a_5, \qquad (17)$$

where E_S is the steric Taft parameter.

In order to take into account the influence of individual substituents on biological activity, i.e. in order to examine a series of compounds and also to calculate the values of $\lg P$ for substances which have not as yet been investigated, the substituent constant $\pi_X = \lg(P_X/P_0)$ was introduced by analogy with σ.[52] Here P_0 is the partition coefficient of the unsubstituted initial compound in a model system and P_X is the partition coefficient of the compound with the substituent X. It can be shown that π can also be obtained as a result of the application of the PLE to hydrophobic interactions. For a series of substances involved in a reaction j, variation of the substituent X yields

$$\lg(\bar{k}_x/\bar{k}_0) = \varkappa_j \lg(K_{xi}/K_{0i}), \qquad (18)$$

where K_i are the equilibrium constants for the standard reference reaction i, $\bar{k}_j$ are the rate constants for reaction j (K_{Xi} and $\bar{k}_{Xj}$ when the molecule contains the substituent X and K_{0i} and $\bar{k}_{0j}$ in its absence), and κ_j is the constant of reaction j. The type of interaction between the substituent and the reaction centre for reactions i and j is assumed to be the same. If the interaction is assumed to be hydrophobic, then evidently the equilibrium constant in a partition system of the oil–water type is none other than the partition coefficient of the substance P. The partition of the substance (i.e. its interaction with the solvent of the "solvation ⇌ desolvation" type with respect to one of the solvents) in the model system, for example octanol–water, may be used as the standard reference reaction. Then substitution of P_X and P_0 for the equilibrium constants K_{Xi} and K_{0i} in Eqn. (18) yields an equation similar to Hammett's equation in which the constant $\pi = \lg(P_X/P_0)$ is analogous to the Hammett constant σ:

$$\lg \bar{k}_x = \varkappa\pi + \lg \bar{k}_0. \qquad (19)$$

Like other reaction constants of the substituents, the constant π depends on the system in which it is determined[41,52], owing to the interaction of the substituents with other parts of the molecule. In practice this is taken into account by selecting for the calculation of π the corresponding model systems (molecules) similar to the molecules analysed.

By definition there is a linear relation between $\lg P_X$ and π_X, which made it possible to employ the corresponding values of π instead of $\lg P$ in equations of type (17):

$$\lg(1/C_0) = a_1\pi^2 + a_2\pi + a_3\sigma + a_4E_s + a_5 \quad . \qquad (20)$$

These can be calculated[41,52].

In contrast to the kinetic approach constituting the basis of Hansch's method, Franke and Oehme[8] described an attempt to obtain similar structure–activity relations on the basis of an equilibrium model. It is assumed in this case that the entire chain of chemical reactions leading to the final biological effect operates only in the establishment of the equilibrium at each stage. Thus the entire system may be characterised by the overall equilibrium constant

$$K_c = \prod_i K_i, \qquad (21)$$

which describes the equilibrium between the initial state (active substance D + receptor R) and the final state, identified with a "biological stimulus" St, corresponding to the Law of Mass Action. The concentration of the reaction product C_X, which is the main one for the observed biological action, was introduced[8] as a measure of St:

$$St = C_x = K_cC_DC_R. \qquad (22)$$

Subsequently a general equation of type (3) was obtained[8] by expressing the biological activity $[A]$ in the form

$$[A] = f(St) = f(K_cC_DC_R), \qquad (23)$$

taking into account the linear sections on the dose–activity curves, where

$$[A] = kSt, \qquad (24)$$

and introducing the transfer functions W (analogous to the function N in Hansch's method) in order to find the concentration of the active substance near the receptors. Eqns. (16), (17), and (20) are special cases of the type (3) equation. It is readily seen that in this case the use of Eqns. (21)–(24) constitutes a formal procedure which makes it possible to bring the physicochemical parameters determining K_C and W into correspondence with $\lg[A]$ or $\lg(1/C_0)$.

It is clear from the foregoing that there is at present no unique physicochemical theory corresponding to both the kinetic and equilibrium approaches. However, an attempt may be made to group the physicochemical features of compounds in accordance with their physical significance in order to take into account to the maximum possible extent the structural characteristics responsible for the biological activity shown by the compound. In many instances this facilitates the interpretation of structure–activity correlations and gives them a concrete physicochemical content.

We shall consider certain possibilities of a group of parameters (based on their physical significance) for the derivation of correlations. According to Eqn. (5), when N is expressed in terms of hydrophobic properties of the substance, then

$$\lg [A] = \lg (1/C_0) = f'_h(S_h) + f_e(S_e) + f_s(S_s) + \text{const}, \tag{25}$$

where f'_h is a function combining the partition phenomena and the hydrophobic interaction with the receptor.

Not only physicochemical parameters of the entire molecule but also certain substituent constants may be chosen as the S_i in Eqn. (25). The following parameters can be used under these conditions.

(1) as S_h: (a) $\lg P$ [11,12,41,48,53] or quantities associated with it—the Hansch constant π (the lipophilicity parameter)[11,12,41,52]; $R_M = (1/R_f - 1)$ or ΔR_M (analogue of π) from thin-layer partition chromatography[54-56]; the protein binding constants (determined for a model system)[12,41,57,58]; $\lg C_s$§, where C_s is the solubility in water[42,58,59]; (b) quantities related to molecular size and packing: the molar volume (V_M), the parachor (Pr), molar refraction (MR), the solubility parameter (δ), the diamagnetic susceptibility (χ_m), the molecular connectivity (χ),[42,60-67], and the molecular weight M [60]; (c) the molar attraction constant (F_a) [60,63,64]; (d) the hydrophilic–lipophilic balance (HLB) [68];

(2) as S_e: (a) different electronic substituent constants σ characterising the electron density at the reaction centre[8,11,12] if they can be expressed[69] as a linear combination of the constants $\mathscr{F}$ and $\mathscr{R}$, where $\mathscr{F}$ is the inductive constant, which takes into account only the inductive effect of the substituent on the functional group and $\mathscr{R}$ is the resonance constant, taking into account all the resonance interactions (the use of $\mathscr{F}$ and $\mathscr{R}$ [70-72] makes it possible to avoid the consideration of different types of σ in the correlation equations)¶. (b) The charge-transfer constant (C_T), which is a measure of the stability of the complex formed via charge transfer[78-80]; (c) various parameters characterising the electron density, bond orders, and bond lengths; parameters of the first kind include the changes in the ionisation constant ΔpK,[10,12,81,82] the ionisation potential I,[83] and the polarographic half-wave potential $\varphi_{1/2}$ [84]; parameters of the second kind include the molar electronic polarisation (P_E) [85-87] or simply the polarisability (α),[60,83] the dipole moment (μ),[12,88,89] and spectroscopic data (infrared, ultraviolet, NMR, etc.)[90-98]; (d) various quantum-mechanical parameters (see below).

(3) As S_s: (a) steric Taft constants (E_s),[11,12,99] determined analogously to σ, and the corrected steric interaction parameters $E_s^S = E_s + 0.306(n_H - 3)$ [12,100]; (b) the van der Waals radii (r_V).[37,101-103].

The literature data for structure–activity correlations have shown that the degree of the functions f'_h, f_e, and f_s in Eqn. (25) is as a rule not greater than the second, i.e. in the general case they correspond to a parabolic relation and are therefore characterised by certain extremum values corresponding to S_i^0. The extremum is determined from the condition

$$\left(\frac{\partial \lg (1/C)}{\partial S_{i=k}}\right)_{i \neq k} = 0$$

and corresponds to the optimum value of the corresponding physicochemical parameter for biological activity[10-12,104]. The possibility of an optimum value of S_h^0 can be explained in different ways[104]. It appears that the following most important factors for the occurrence of S_h^0, S_e^0, and S_s^0 may be distinguished: (a) metabolism or competing metabolic reactions in the biological system; (b) the obligatory complementarity of the molecule (or its active component) and the reacting region of the receptor; (c) a low concentration of the active molecules in the vicinity of receptors. Furthermore, in the study of enzymes *in vitro* the occurrence of S_i^0 can be due to micelle formation with entrainment of active molecules.

The number of parameters quoted above may be reduced if they are expressed by a quantum-mechanical procedure. It has been shown[105] that π as well as $\lg P$ can be expressed as a linear function of quantum-chemical parameters:

$$\pi = k_1 \sum_r |Q_r^T| + k_2 \sum_r S_r^E + k_3, \tag{26}$$

where $|Q_r^T|$ is the absolute value of the overall charge, S_r^E is the electrophilicity caused by the superdelocalisation of the electrons at the atom r, and k_1–k_3 are constants.

However, since the use of experimental values of π and $\lg P$ to determine structure–activity correlations yields satisfactory results in individual instances, it appears much more useful to employ quantum-chemical methods in order to express the term $f_e(S_e)$,[12,106-116], using various computational methods[116].

The following quantum-chemical quantities are used as parameters characterising reactivity†: the overall π-electronic charge $q_r(\epsilon)$‡ on the atom r; the overall ($\sigma + \pi$) charge on the atom r; the highest occupied (E_{HOMO}) and lowest unoccupied (E_{LUMO}) molecular orbitals; the electrophilic (S_r^E) and nucleophilic (S_r^N) characteristics of the influence of superdelocalisation[118,119]; the free valence index F_r (mainly for homolytic reactions)[114]; the atomic-orbital coefficient C_r.[120]

In the general case it is not clear which quantum-chemical parameters should be preferred for use in the structure–activity correlations. This depends on the proposed mechanism of the biological action of the compound and is usually related to the charge on the heteroatom (for example q_N on the nitrogen atom), to the energies E_{HOMO} and

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§It has been shown[59] that, in the study of the biological activities of substances introduced into a biological system in a solid form, the rate of dissolution of this form must be taken into account in structure–activity correlations. This is because the correlation between the rate and C_s is poor.

¶In radical reactions it is still necessary to employ $\sigma^{\bullet}$ and E_R, because they are poorly correlated with $\mathscr{F}$ and $\mathscr{R}$.[73-77]

†They are calculated using parameters obtained from spectroscopic measurements, the ionisation potentials, etc. The corresponding values for the extensive Hückel method have been tabulated[117].

‡Here and henceforth the subscript r means that the corresponding quantity refers to the atom r in the molecule.

E_{LUMO} or to the difference $E_{\text{HOMO}} - E_{\text{LUMO}}$, and to S_N.[8,10,12,114,116] Hypotheses of this kind are not often found to be true in practice. This is probably because only the potential reactivity of the compound is considered by this procedure without taking into account the possible steric, conformational, and other parameters influencing the biological activity. Attempts have therefore been made to use various linear combinations of quantum-chemical parameters[114]. However, this procedure has not as yet been adequately investigated and its scope is not entirely clear.

V. ANALYSIS OF THE STRUCTURE-ACTIVITY RELATION BY HANSCH'S METHOD

As stated above, Hansch's method is used to express the biological activities of members of series of related compounds in the form of functions of physicochemical parameters characterising the structure of these compounds. As a rule, the relative importance of taking into account these parameters in the description of biological activity is not known beforehand, which makes it necessary to test a series of model equations containing various combinations of parameters. These equations are obtained by regression analysis, after which the best one is selected on the basis of the significance of the correlation coefficients. It is recommended[8,103] that certain rules be observed.

1. It is desirable to consider the greatest possible number of independent parameters.

2. The parameters S_i considered above are as a rule integral quantities characterising molecular properties in a complex manner; for this reason, there is a definite relation between them. The literature data show that the correlation between the S_i referring to the same interactions (for example to hydrophobic interactions) is much better than between parameters characterising different types of interactions (for example between $\lg F$ and σ).[70,121] This observation can be used as one of the empirical rules for the selection of various combinations of independent parameters S_i§.

3. After the preliminary examination of the possible versions of the set of parameters and comparison with the aid of regression analysis of a series of model equations, it is necessary to determine by means of Student's t distribution the levels of significance of individual coefficients. Parameters with a low level of significance are disregarded.

4. The multiple regression coefficient[122,123] R, the standard deviation, and the F test are used for the statistical assessment of the equations obtained. The square of the correlation coefficient (R^2) indicates the proportion of variations in data obtained from the corresponding equations. The closer it is to unity, the closer the functional relation obtained to the one sought. For similar values of R, it is necessary to take into account the standard deviations and to use equations with the smallest standard deviations. The F test is used to estimate the probability that the suitability of a particular type of equation is not fortuitous.

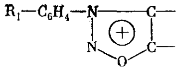
5. In order to exclude random correlations, it is recommended that at least five-six results of biological measurements are obtained for each physicochemical parameter tested[124].

6. Other conditions being equal, preference should be given to simpler equations.

7. In order to reduce the amount of calculations, to simplify them, and to avoid fundamental errors, it is necessary to take into account the reality of the mechanism of the phenomenon under consideration (see Section VIII), since it is possible to obtain on the basis of formal characteristics equations with satisfactory values of R^2 and a high significance according to the F test but having little in common with reality[125].

If possible, one should divide the substances compared into a series of definite substructures with common features, for example, substances with *cis*- and *trans*-positions of a certain group, series obtained by changing one substituent while those in other positions are kept constant, etc.[8] Such subdivision naturally simplifies the problem (a similar empirical approach was discussed in Section III). In order to derive equations for such a series of compounds, it is necessary to introduce an auxiliary parameter D, taking into account the difference between the substructures. For example, it has been used to take into account the steric difference between the *meta*- and *para*-derivatives of diethyl phenyl phosphate in the inhibition of cholinesterase[126]—it was set equal to unity for the former and to zero for the latter. The value of n_H, the number of hydrogen atoms linked to a definite atom in the molecule, for example, the nitrogen atom of an amino-group, may be chosen as D.[127] The auxiliary parameter may be used to combine equations taking into account the differences between the subgroups in order to determine the biological activity of particular stereoisomers only. In those cases where there are several subgroups, it is possible to introduce two or more auxiliary parameters[128].

Examination of polysubstituted compounds presents the greatest difficulties. In such cases it is not always possible to obtain an equation describing the correlation between the biological activity and the sum of identical substituent constants i.e. ($\sigma_i + \sigma_j$, $\pi_i + \pi_j$, etc.), because the influence of different types of substitution may have different effects on the biological activity. This problem is solved by substituting in the equation parameters characteristic of the particular type of substitution. For example, in describing the inhibition of oxidative dealkylation by compounds having the general formula



an equation with a high correlation coefficient is obtained only when the constants π and σ are taken into account separately for R_1 and R_2.[129]

The most complex case obtains when the biological activity of substances is influenced appreciably by their metabolism.

VI. THE QUANTUM-STATISTICAL APPROACH

Attempts to relate the biological activity of a substance to microscopic characteristics of the interactions in the substance-receptor system by a combination of quantum-statistical and statistical thermodynamic methods have been undertaken[94,130,131]. In order to obtain a working

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§ In order to characterise the absence of a relation between physicochemical parameters, the so called individual correlation coefficients r, determined as dimensionless quantities, varying in the range $-1 \leq r \leq 1$, are used. The closer the value of r to 0, the more independent are the corresponding physicochemical parameters.

model, the following assumptions were made: (1) in a multistage process occurring from the instant of the introduction of the substance into a biological system until its interaction with the receptor resulting in biological activity, the probability of each stage is independent of that of other stages; (2) substances reach the sites of reception by virtue of Brownian-like motion; (3) the reaction sites consist of localised atoms; (4) the binding of the biologically active substance at a single receptor or group of receptor sites is independent of its binding at other sites in the system.

According to these hypotheses, the initial equation can be expressed in the form

$$\frac{d[BR]}{dt}=KC_0p_1p_2, \tag{27}$$

where K is a proportionality coefficient, C_0 the initial concentration of the substance, p_1 the probability of the completion of the stage involving the penetration of the substance to the receptor, and p_2 the probability of the binding of the substance to the receptor. Next is is postulated that p_1 varies in parallel with the parameter π, i.e. with the lipophilic properties, which are responsible for the passage of the substance through biological membranes,, and that p_2 varies in parallel with the adsorption of the substance at the receptor site or group of sites. If it is assumed that the binding of the substance to the receptor occurs at energetically indistinguishable sites, then p_2 should be wholly determined by the electronic structure of the heteroatoms of the substance adsorbed. For the specific examples which have been examined[94,131], it was postulated that the binding takes place via a carbonyl group, the energetic characteristics of the probability of the binding of which to receptors were determined from spectroscopic data.

The mathematical expression[131] relating the activity of the substance to the permeability of membranes to it and the probability of its interaction with the receptor includes the following parameters: the lipophilicity, the spectroscopically estimated distribution of the potential reactive centres (groups), and the chemical potential of the test substance in solution. It follows from the analysis of this expression that the most active compound may be found or synthesised when the substituent or its position in the molecule is chosen in such a way that it influences simultaneously the lipophilic properties of the compound and the energy state of the reactive group.

Insufficient reliable data are as yet available for the assessment of the predictive power of the method[130]. At the present time one can estimate only its fundamental advantage: the necessary parameters—the lipophilicity and the wavenumbers of the suggested reactive groups—may be determined experimentally fairly readily.

VII. THE USE OF FACTORIAL ANALYSIS IN THE DERIVATION OF STRUCTURE-ACTIVITY RELATIONS

Evidently the limitation of the above methods to any one type of biological activity is artificial. In order to solve rigorously the problem of the relation between structure and activity, it is necessary to take into account all possible physiological processes and to relate them to the entire set of physicochemical parameters characterising or determining each stage in the action of the given substance. The difficulties in this procedure are the unusual complexity of biological systems, the wide variety of reactions occurring in them, and the imperfection of our knowledge of their mechanisms and interrelations. Virtually the first attempt to take into account several possible versions of the interaction is a study[132] where the method of factorial analysis was used.

Mathematical factorial analysis may be formally applied to any complex multidimensional problem, provided that it can be represented by a sum of interrelated functions of certain variables, i.e. in the form

$$P(i,k)=\sum_{j=1}^{m}U(i,j)V(j,k), \tag{28}$$

where $P(i,k)$ is the measured property of the system in the ith case when k is varied, $U(i,j)$ is the jth factor for the ith case, and $V(j,k)$ is the jth variable factor for the given variable k; the summation is carried out with respect to all the factors j which are important[132]. In the relevant specific instance of the structure-activity relation, we have

$$[A](i,k)=\sum_{j}D(i,j)H(j,k), \tag{29}$$

where $[A](i,k)$ is the kth measured biological activity of substance i, $D(i,j)$ the jth property (physical or chemical) of the ith compound, and $H(j,k)$ the jth parameter (physiological) of the kth biological activity; the summation is carried out with respect to all j independent parameters which are necessary to take into account the results of tests.

The form of factorial analysis applied to the case described differs from the standard form by the fact that it includes the method of regression analysis as one of the factors[132,133] in the form of the identity factor. Thus, provided that the accuracy of the experimental data is known, it is possible to determine the number of independent abstract factors ("eigenvectors" according to Weiner and Weiner[132]) necessary for the complete characterisation of the factorial space, i.e. one can determine the number of variables influencing the system tested. Leaving on one side the discussion of the mathematical formalism used by Weiner and Weiner, we shall mention only that in this first stage the number of eigenvectors is equivalent to the dimension of the factorial space. The next step is the identification of each factor in the form of the specific level of its significance for each physiological response. For this purpose, the entire set of variables is compared with all possible physicochemical properties or parameters of the model interactions which are presumed to be important. Although Weiner and Weiner[132] used the characteristics of substances usually employed for semi-empirical models, this does not imply that one must necessarily employ the polarisability, the partition coefficients, etc. (Table 1).

Since the term $[A](i,k)$ in Eqn. (29) may be expressed and measured experimentally as the biological activity manifested in a kth case and the term $H(j,k)$ relates any physiological parameter to any property of the substance and the quantity $[A]$, the method of factorial analysis may be used to predict the uniqueness of the compound tested or to specify the set of properties giving rise to the maximum useful activity for a minimum number of side effects. The method of factorial analysis was tested by comparing the calculated data with the experimental results obtained by measuring the activities of 16 substances in a series of substituted compounds having the general formula $R_1-\overset{|}{N}-R_3$ in 11 types of biological and physiological action (including action on a specific type of activity, the antagonistic behavioural reflexes of the animal, and objective parameters of the state of the organism). It was established[132] that, in order that the model should reproduce the results of studies to within ±0.1 on a logarithmic scale, it is necessary to employ eight parameters describing, according to Weiner and Weiner[132], the main structural characteristics of substances. Unfortunately, a list of the properties employed is not given[132]; nevertheless the potential possibilities of this approach should stimulate the expansion and intensification of this field of research.

VIII. THE USE OF SEMIEMPIRICAL METHODS IN THE STUDY OF THE MECHANISMS OF REACTIONS OF BIOLOGICALLY ACTIVE SUBSTANCES

Apart from the selection of the optimum compounds, it is desirable to obtain, as a result of the analysis of the structure–activity relation, an idea about the mechanism of their biological activity. We shall consider one of the possible procedures for this purpose.

1. The conclusion as to which properties of the substances are the most important for their biological activity may be reached on the basis of the statistical significance of the physicochemical parameters in correlation equations.

2. Next one must determine the ways in which these properties influence the biological activity, beginning with the form of the function $f_i(S_i)$ [Eqn. (25)]. Here account must be taken of the fact that a parabolic form of the relation with $\lg P$ (or with other S_h) may be a consequence not only of the partition of the substance between the phases[12,134] but also of its hydrophobic binding to the receptor[58]. Because of this, only in the case of a linear relation with $\lg P$ can one conclude that hydrophobic binding is in fact the determining process[8].

In certain cases where a cross-product of terms of the type S_iS_j is introduced in Eqn. (25), the correlation is improved[10,135]. If S_i and S_j are substituent constants referring to a single type of interaction, such cross-product takes into account the mutual influence of the substituents[50]; otherwise, it takes into account the mutual perturbations of different types of interaction[8].

3. When the influence of hydrophobic binding is decisive, one can estimate approximately the dimensions of the binding region on the receptor from the values of the parameters S_h for which a discontinuity is observed in the functional dependence of $[A]$ on S_h.[58]

4. Certain conclusions about the mechanism of the motion of a given substance may be reached by analysing auxiliary parameters, which must be included in the equation to improve the correlation.

5. If possible one should calculate $\lg P_{op}$ (or the values of other S_h^0) and compare them with the corresponding values for other series of compounds giving rise to a similar biological response. For example, similar values of $\lg P_{op}$ obtain for a non-specific action of the substance. In particular, in the case of narcotic action identical values $\lg P_{op} \simeq 2$ were obtained for a series of substances with fundamentally different structures and compositions: barbiturates, thiamorpholidines, acetylenic alcohols, acetylenecarbamates, etc. This permits the conclusion that narcosis is due to a non-specific action by the substances and that substances with $\lg P_{op} \simeq 2$ are in general the most effective narcotics[12].

An approximate model of the biological activity of the substance may be obtained from the information derived by the above procedure but must be subsequently tested and refined by additional experiments.

Interesting prospects for the understanding of the mechanism of the most complex stage in the interaction of the substance in the organism—the formation of a complex with the receptor—arise from a theoretical treatment of Hansch's method[36,120]. Since the experimental determination of the type of substance–receptor bond is difficult, it has been suggested that the total energy change ΔE occurring on formation of the substance–receptor complex be used as a bond characteristic. If one considers a series of substances with the same type of biological activity, which is due to binding to particular receptors, then the difference between the activities of these substances may be expressed to a first approximation by the change in the free energy of formation of the substance–receptor complex:

$$\Delta[A] = -\left(\frac{1}{RT}\right)\Delta G + \text{const}, \qquad (30)$$

where $\Delta G = \Delta E + \text{const}$.

ΔE represents, according to the authors[36,120], the sum of the independent contributions of the electronic (ΔE^e), solvation (ΔE^d), steric (ΔE^s), and conformational (ΔE^p) components of the energy change. This hypothesis corresponds to a linear relation between the free energies[36]. The next problem is to express the different contributions ΔE^i in terms of experimental or calculated quantities. In order to calculate ΔE^e, for example, using the perturbation theory[136,137], we obtain

$$\Delta E^e = \sum_r \sum_s E_{rs} = \sum_r \sum_s \Bigg(\underset{\text{(I)}}{-\frac{Q_r Q_s e^2}{D_{rs} R_{rs}}} + \underset{\text{(II)}}{\sum_m \sum_n \frac{2C_{mr}^2 C_{ns}^2 \bar{\beta}^2}{E_m^* - E_n^*}} \Bigg), \qquad (31)$$

where E_{rs} is the electronic energy of the interaction between atoms r and s, Q_r and Q_s are the overall charges, e is the electronic charge, R_{rs} is the distance between atoms r and s, D_{rs} is the dielectric constant of the medium, $E_m^* - E_n^*$ is the energy difference between the highest occupied molecular orbital of the receptor and the lowest unoccupied molecular orbital of the compound, β is the exchange integral taking into account the interaction between the molecular orbitals, and C_{mr} and C_{ns} are the atomic orbital coefficients. Each pair of interacting atoms, in a molecule of the compound (s) and the receptor (r) is assumed to make an independent contribution to ΔE^e.

Since Eqn. (3) includes properties characterising the receptor, it cannot be used directly. For this reason, limiting cases are considered[36,120], corresponding to different relations between E_m^* and E_n^* in Eqn. (31).

1. The Case "Controlled by the Boundary"

If $E_m^* \simeq E_n^*$, the interaction between the corresponding orbitals is decisive for E_{rs}. Then term (I) can be neglected in Eqn. (31) compared with term (II). This case corresponds to the formation of a covalent bond between the molecules of the substance and the receptor. In order to determine the necessary properties corresponding to the receptor, it was suggested that, for a series of related compounds combining with the same receptor site, the coefficients C_{mr} are constant for each compound. Because of this we have

$$\Delta E^e = \sum_s a_s C_{ns},$$

where α_s includes C_{mr}. The following final expression is obtained for ΔE taking into account the solvation energy $\Delta E = \Delta E^e + \Delta E^d$:

$$\Delta E = \sum_s (\alpha_s C_{ns} - \lambda_{ns} Q_s \pm \lambda'_{ns} Q_s^2), \tag{32}$$

where, as mentioned above, the α_s are approximately constant for a series of substances interacting with the same receptor, while λ_{ns} and λ'_{ns} are constants obtained by examining ΔE^d.

An example of the correlation between $\lg(1/C_0)$ and the parameters included in Eqn. (32) is provided by the equation

$$\lg(1/C_0) = 8.8 C_{nN} + 237 Q_N - 1670 Q_N^2 + 6.6, \tag{33}$$

obtained for the bacteriostatic activity of sulphonamides against *E. Coli* [120]. The subscript N in Eqn. (33) refers to the nitrogen atom.

2. The Case "Controlled by the Charge"

This obtains if the difference between E^*_m and E^*_n is large. Then term (I) in Eqn. (31) is of decisive importance, compared with terms (II), and the interaction between atoms r and s is determined mainly by the total charges Q_r and Q_s. In this type of interaction the bond between the compound and the receptor is ionic. When account is taken of this factor, Eqn. (31) can be written as follows:

$$\Delta E = \sum_r \sum_s \left[-\frac{Q_r Q_s e^2}{D_{rs} R_{rs}} + 2\left(\sum_m C^2_{mr}\right)\left(\sum_n C^2_{ns}\right)\gamma \right], \tag{34}$$

where γ is the average value of the ratio $\beta^2/(E^*_m - E^*_n)$. Having assumed the constancy of C_{mr} and Q_r in relation to C_{ns} and Q_s respectively for a series of related compounds interacting with the same receptor and taking into account the fact that ΔE^d in the case controlled by the charge is zero, it is possible to obtain the following equation [36]:

$$\Delta E = \Delta E^e = \sum_s (\nu_{ns} Q_s + \xi_{ns} S_s^E), \tag{35}$$

where ν_{ns} and ξ_{ns} are constants and S^E_s is the parameter of the capacity for ultradelocalisation (see Section IV). The case commonest in practice is probably intermediate between the boundary cases examined above. It has been suggested that the following expression for ΔE be used for it [36]¶:

$$\Delta E = \Delta E^e + \Delta E^d = \sum_s (\nu_{ns} Q_s + \xi_{ns} S_s^E) + h \lg P. \tag{36}$$

The parameter π may be expressed similarly in terms of quantum-chemical characteristics [105] (see Section IV). Without considering the scope of Cammarata's method in the determination of biological activity, which is clearly limited by the complexity of the calculations, one must emphasise yet again that the principles underlying it may be productive in the treatment of the mechanism of the formation of the substance–receptor complex.

IX. THE SCOPE OF PRACTICAL APPLICATIONS, ADVANCES, DIFFICULTIES AND PROSPECTS

As can be seen from the foregoing discussion, there exist at present a number of approaches to the solution of the problem of the correlation between structure and activity, of different complexity and developed to different extents. They are compared in Table 2—the principles underlying the methods, their applications, and certain disadvantages are indicated. The practical value of correlations usually depends on three factors [138]: accuracy, simplicity, and the type of information necessary for use in an empirical equation. Evidently, as regards the "accuracy and simplicity" criteria, preference cannot be given to any one of the approaches described and only the future will show whether the apparently most progressive method of factorial analysis will justify itself. If the existing approaches are considered from the standpoint of the information employed in them, then in an implicit (additive model, substructure analysis) or explicit (factorial analysis) form such information can be expressed in terms of one of the specific types of the multiparameter regression model. Indeed it has been shown [139] that there is a relation between the contribution of substituents to biological activity and their physicochemical characteristics (the substituent constants π, σ, etc.), i.e. all the models enumerated contain common information, which is most clearly expressed in Hansch's model. This makes it possible to consider different approaches from the same standpoint and to justify to a large extent the attention which has been devoted in the literature to the multiparameter regression model.

More than 2000 equations of types (16), (17), and (20) for more than 20 000 chemical compounds have now been described [140]. Many of these have all the formal features (high correlation coefficients and statistical levels of significance) which at first sight permit the conclusion that a change of the substituents in the structure alters its hydrophobic, electronic, steric, and other properties, and hence the biological response elicited by the compound. According to Hansch's method, the last factor may be taken into account and expressed mathematically by the summation of the physicochemical properties of the substituted compounds. Approximately 50 relations, which have been used to predict the efficiency of the biological action of substances, are quoted in the literature [98,141–143]; the structure–activity correlatons are used much more widely to discover the mechanisms of the action of biologically active substances (see, for example, Refs. 8, 10–12, 18, 36, 95, 144, 145). The following causes responsible for a certain gap between theory and practice may be suggested.

1. The resultant biological activity of substances depends on their influence on many physiological processes occurring in the organism. The experimental limitation of the above method to any one type of biological activity, expressed in terms of the concentration of the substances giving rise to the given effect, is therefore too rough an approximation to reality to be used as a parameter. It appears that, only for a reliably established mechanism, for example, when the latter is determined by a particular enzyme, can the concentration of substances giving rise to a standard change in the concentration of the enzyme be used correctly to calculate $[A]$ in terms of the corresponding properties and characteristics of model interactions.

¶In Eqn. (36) $\lg P$ may be replaced by π.

Table 2. Principal methods for the determination of structure–activity correlations.

Method	Principle (hypothesis) underlying the method	Field of application	Disadvantages	Remarks
Mathematical additive model	The effectiveness of the biological activity of the chemical compound is determined by its structure and may be calculated as the sum of the contributions of the substituents in its molecule, the contribution of each substituent being independent of the presence of others (hypothesis of the additivity and independence of the contributions of substituents)	Prediction of the effectiveness of the biological activity in series of related compounds and hence reduction of the number of biological tests	Is inconsistent with the ideas concerning the influence of substituents on one another and hence on the physicochemical properties of the molecules of the given substance. The method is applicable only to series of compounds with the same type of biological activity	In order to improve it, the model may be (a) modified to take into account the mutual influence of substituents and (b) may be related to the multiparameter regression model. In both cases the model becomes considerably more complex
Substructural analysis	Arbitrary structural elements (fragments) are characterised by the frequency of their repetition in known biologically active compounds. The compound tested is analysed from the standpoint of the presence of such fragments. (Hypothesis—the biological activity of the substance is determined by the presence of particular structural elements.)	Non-experimental screening—prediction of the direction and effectiveness of the biological activity of substances. Determination of original structures	Has no physicochemical basis. The quantitative predictions of the effectiveness of biological activity are unreliable	In order to improve quantitative estimates, physicochemical characteristics of substances are introduced—this version of the procedure is referred to as the pattern recognition method
Multiparameter regression method	The set of parameters characterising model physicochemical processes occurring with participation of the given substance is correlated with its biological activity. (Hypothesis—the biological activity is determined by the structure and reactivity of the molecules of the given compound)	Prediction of the effectiveness of biological activity in series of related compounds without biological tests. The study of the mechanisms of biologically important chemical reactions	Is applicable to series of compounds. Does not allow the prediction of the direction of biological action. Conclusions concerning the effectiveness of substances are frequently erroneous	In order to reduce the number of parameters, one can use calculated or experimental quantum-chemical parameters—the quantum-statistical approach, the Cammarata method.
Factorial analysis	Relates the characteristics of the structure of the compound to the set of possible physiological results of its action. By sorting the possible variants, it established the ways in which the biological activity of substances arises and determines its effectiveness	Non-experimental screening—prediction of the direction and effectiveness of biological activity. Prediction of the uniqueness of the structure and form of activity and of side effects	Complexity. The scope of the method has not been adequately tested	Includes the multiparameter regression model as one of the factors

2. Apart from its evident advantages, the extensive application of mathematical statistical methods, which is characteristic of semiempirical approaches, to the structure-activity problem made the true pathways followed in the biological action of substances and reliable results statistically insignificant against the background of the enormous number of the results of biological tests obtained by different investigators. The low accuracy and reproducibility of biological experiments naturally have an effect under these conditions.

3. The use of regression methods to obtain correlation equations requires much greater caution than is frequently exercised in the literature. It is known that a number of independent variables can be correlated successfully using random terms if the latter are also independent. In reality, this situation means that our information about the mechanisms and the ways in which a particular type of biological activity is manifested is still insufficient to take into account the maximum number of parameters important for the manifestation of biological activity.

The above difficulties are fundamental and an attempt has been made only recently to eliminate some of them by means of factorial analysis[132]. Nevertheless there is at present no alternative to Hansch's method and its different versions in the formulation of quantitative structure–activity relations. This is mainly because the foundations of Hansch's method rest on the most general physicochemical principles, which probably serve as the basis of the mechanism of the action of biologically active compounds.

X. CONCLUSION

Summarising the foregoing review, it appears useful to put forward certain considerations applicable to the problem as a whole. The above methods for the determination of the types of functions relating quantitatively the characteristics of the structure of a substance and its biological activity are a natural consequence of the theoretical foundations of these methods and the types of interactions (in the set of all possible interactions) in the substance–biological object system which are taken into account.

It has been established reliably that the best correlation between biological activity in a series of substances and the partition coefficient ($\lg P$), the lipophilic constants of the substituent (π), and other characteristics associated with them is shown by substances exhibiting a non-specific type of biological action[†]. This implies that the chemical reaction which determines the outcome of the action of the substance occurs on the surface or within the cell membrane and that the site of the effective action of the compound is not localised. In practice such simple behaviour is probably rarely encountered.

[†] For example, it has been suggested[60] that a satisfactory correlation between $\lg P$ and π be used as a criterion for the estimation of the non-specificity of the biological action of the substance.

It is quite evident that the value of any structure–activity relation, not including the specificity characteristics as a factor of the manifestation of biological activity, is low. However, in the case of the specific binding of substances it is at present impossible to specify the number and types of parameters whose combination would be sufficient for an exhaustive and general solution of the problem of the determination of the structure–activity relation. This factor probably in fact explains the number of different parameters and their combinations (Table 1) which have been used to establish correlations and which are in essence difficult to extend further. It would appear that a satisfactory description of a theoretical relation in terms of experimental data should indicate that the model adopted reflects correctly the essential features of real processes and that the leading role among them is played precisely by those interactions which are taken into account in the corresponding correlation. Nevertheless, "astonishing freaks" in Hansch's words[146] (i.e. equations which are unrealistic in terms of their physical significance or ineffective in their predictive power but have high correlation coefficients), are discovered all too often when the results of empirical and semiempirical approaches are tested, which indicates most clearly certain significant miscalculations underlying the derivation of the corresponding equations. Whether this situation is a consequence of the impossibility of allowing completely for the entire set of different types of interactions between the substance and the organism and the lack of clear-cut principles whereby each specific situation can be reduced to a single equation of all the necessary parameters, or whether it is due to other less evident causes, is difficult to establish. Apart from the objective complexity of the problem, we believe that this is aggravated by the excessive employment of different versions of the approaches described above, frequently without adequate critical analysis of the results of biological tests used and the selected physicochemical parameters.

Future progress in the application of the procedures, outlined above, for the determination of quantitative structure–activity relations will probably be achieved by setting up a few fundamental experiments in combination with their profound theoretical elaboration and not by the excessive accumulation of new results. Furthermore, the main task—the parametrisation of biological activity, which cannot be regarded as finally completed in the form which exists at the present time—remains of primary importance.

In this connection it appears that real advances in the semiempirical approaches may be expected as a result of the narrowing of their fields of application, for example by restricting them to those cases where a definite type of biological activity may be characterised by the behaviour of molecular-biological, biochemical, and other models, and not by their limited extension to all types of biological activity *in vivo*.

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The above review covers the literature up to 1975 inclusive. Among the papers published recently, mention should be made of the reviews on the mathematical additive model[286-287], the relations between this model and the multiparameter regression method (MRM),[287] the possibility of using the parachor in correlations between the chemical structures and biological activities of substances[288], a new "bilinear" model for a non-linear relation between the biological activities and hydrophobic properties of molecules[290], model equations for MRM for substances capable of ionising[291], a classification of therapeutic agents in conformity with pharmacophors for the pattern recognition method[292], the elucidation of the relative importance of steric parameters in relation to steroid hormones[293], and a compilation of tables of lipophilic parameters[294].

It has been suggested that new parameters be used in MRM: partition coefficients taking into account both the neutral and ionic forms of the given substance[295]; surface activity and the work of adsorption from the aqueous phase at the oil–water interface[296]; "hydrogen bonding" parameters[297]. Increasing attention is being attracted by different modifications of the capacity for molecular binding, which is readily susceptible to calculation whatever the complexity of the given compounds[298,299].

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Bifunctional Catalysis

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The present state of the problem of bifunctional catalysis is considered and the influence of all possible factors (the structures of the reactants and catalysts, temperature, the properties of the medium, etc.) on the efficiency of bifunctional catalysts is discussed. The general characteristics of both the simplest bifunctional catalysts and enzymes are specified.
The bibliography includes 119 references.

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I. INTRODUCTION

The concept of "polyfunctional catalysts" is nowadays fairly broad: substances of this kind may include both the simplest bifunctional compounds, such as acetic acid or 2-hydroxypyridine, and highly organised natural products such as enzymes. It is natural to suppose that all catalysts of this type have certain general properties, the determination of which for the simplest systems will make it possible to understand the characteristics of more complex systems. In other words, a low-molecular-weight bifunctional catalyst can be to a certain extent regarded as the simplest model of an enzyme, as has been frequently noted in the literature (see, for example, Refs. 1–4). There is no doubt that an increase in the complexity of the structure of a polyfunctional catalyst (for example, an increase of the number of groups involved in catalysis or an increase of the number of structural fragments in the skeleton to which the groups are attached) should lead to more or less significant changes in the mechanism of catalysis.

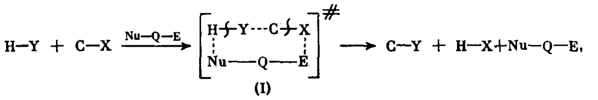
The problem of bifunctional catalysis by comparatively simple molecules is nowadays increasingly closely related to problems of polyfunctional catalysis by complex substances (polymeric catalysis, micellar catalysis, enzymatic catalysis). The ideas about bifunctional (and polyfunctional) catalysis are based on views developed by Lowry and Faulkner[5] as early as 1925 concerning the so called concerted catalysis, according to which two catalysts, acidic or basic, or in the general case electrophilic and nucleophilic, can act simultaneously on different parts of the reactants:

$$\mathrm{HY} + \mathrm{C{-}X} \xrightarrow{\mathrm{Nu+E}} \mathrm{Nu} \ldots \mathrm{HY} \ldots \mathrm{C{-}X} \ldots \mathrm{E} \rightarrow \mathrm{C{-}Y} + \mathrm{HX} + \mathrm{Nu} + \mathrm{E}, \quad (1)$$

where Nu and E are respectively the nucleophilic and electrophilic catalysts accelerating the displacement by the

HY molecule (a nucleophile) of the species X (a nucleophile) being eliminated from the electrophilic molecule C–X.

In 1938 Shilov[6] put forward the following idea about bifunctional catalysis. If two catalytic groups (Nu and E) form part of the same molecule and are located in a rigorously defined manner, then such a catalyst should be more effective than in the case where the two groups form part of different molecules. As we shall see below, this idea proved to be extremely fruitful. It was tested experimentally[7] in the catalysis of the mutarotation of tetramethylglucose (TMG) in benzene by 2-hydroxypyridine. It was found that the activity of 2-hydroxypyridine is much higher than that of a mixture of phenol and pyridine at the same concentration despite the fact that 2-hydroxypyridine is inferior to the monofunctional compounds as regards both acidic and basic strength. The high efficiency of such catalysis can be accounted for solely by its bifunctional nature and the formation of cyclic transition states† of type (I) (general scheme):

 (2)

$$\mathrm{H{-}Y} + \mathrm{C{-}X} \xrightarrow{\mathrm{Nu{-}Q{-}E}} \left[\begin{array}{l} \mathrm{H}\!\nmid\!\mathrm{Y}\cdots\mathrm{C}\!\nmid\!\mathrm{X} \\ \vdots \qquad\qquad \vdots \\ \mathrm{Nu{-}{-}Q{-}{-}E} \end{array}\right]^{\#}_{(\mathrm{I})} \longrightarrow \mathrm{C{-}Y} + \mathrm{H{-}X} + \mathrm{Nu{-}Q{-}E}, \qquad (2)$$

where Nu–Q–E is the bifunctional catalyst;

$$k_E + k_{Nu} \ll k_{Nu\text{-}Q\text{-}E}, \qquad (3)$$

where k are the corresponding rate constants, the subscript to which indicate the nature of a particular reaction. The involvement of cyclic transition states of this kind in the catalytic step should lower the energy barrier to the reaction (see Syrkin[8] and Section IV below) because electron transfer via the ring prevents a significant charge separation. The latter favours the reaction in a non-polar medium, which, as will be shown below, has also been confirmed experimentally.

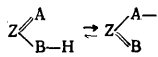
Towards the end of the 1950s and particularly in the early 1960s, studies on bifunctional catalysis were expanded. The following examples of reactions for which the action of bifunctional catalysts has been investigated more or less systematically may be quoted: the mutarotation of monosaccharides[7,9–16], enolisation reactions and processes in which enolisation is the stage activating the reactants (condensation, halogenation, etc. reactions)[17–31], reactions involving nucleophilic substitution at aromatic[32–36] and carbonyl carbon atoms (see, for example, Litvinenko[37] and other references to work by the authors of the present review) and peptide synthesis[38–41].

We believe that, on the basis of the analysis of the studies carried out to date all bifunctional catalysts can be divided into three conventional classes differing in the nature of the action of the catalyst and the type of bond formed between the catalysts and the reactants in the course of the catalytic process.

II. TYPES OF BIFUNCTIONAL CATALYSTS

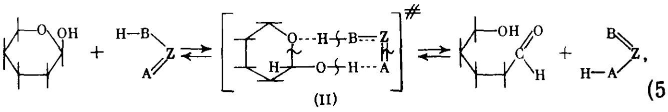
1. Tautomeric Bifunctional Catalysts

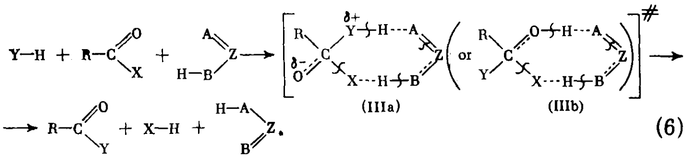
This term was introduced for the first time by Rony in 1969[11]. Catalysts of this type include all compounds which contain functional groups with opposed properties (nucleophilic and electrophilic) and which are involved in a tautomeric transformation of the catalyst:

 (4)

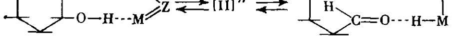
where Z is usually a carbon atom (but it can also be S, P, etc.), or a group of carbon atoms in a chain of conjugated bonds and forming part of the catalyst molecule, and A and B are usually O, S, or N. Such substances include carboxylic acids, their thio-analogues, sulphonic, sulphinic, phosphinic and other organophosphorus acids, derivatives of arsenic acid, 2-hydroxypyridine and analogous compounds, pyrazoles, etc. They are effective as catalysts when a proton has to be transferred during the reaction from one section of the reactant–substrate reaction complex to another, which promotes, overall, electron redistribution in the system and hence the reaction. The above catalysts have yet another characteristic feature—they are capable of forming hydrogen-bonded dimers (see, for example, data on the dimerisation of carboxylic acids[43], benzenesulphonic acid[43], 2-hydroxypyridine[44], and pyrazole[45]). The experimental facts show that substances incapable of such dimerisation usually do not exhibit bifunctional catalytic activity.

Catalytic activity is characteristic solely of the monomeric form of the catalyst. The formation of dimers blocks the functional centres of the catalyst and thus prevents the catalytic process, reducing the concentration of the active form of the catalyst[12,15,46,47]. The mechanism of the action of catalysts of this kind can be demonstrated in relation to the mutarotation of a monosaccharide or nucleophilic substitution at a carbonyl carbon atom:

 (5)

 (6)

Here R = aryl (Ar), alkyl (Alk), or R′CONHR″CH$_2$, X = halogen (Hal), RO, RS, RCO–O, etc., and Y–H = H$_2$O, ROH, RNH$_2$, ROCOCHR″NH$_2$, etc. In all cases bifunctional catalysts form associated species with the reactants via hydrogen bonding, which precede the cyclic transition states (II) or (III) and have structures similar to theirs. For example, the catalytic mutarotation of TMG can be represented as follows:

 (7)

2. Covalent Bifunctional Catalysts

A characteristic feature of catalysts of this type is that, on interaction with the substrate, they form covalent bonds. Here we shall quote several examples of the hydrolysis of esters R′COOR and chloroalcohols as well as the elimination of 3-phosphoglyceraldehyde.

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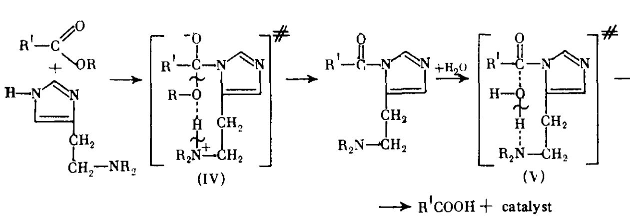
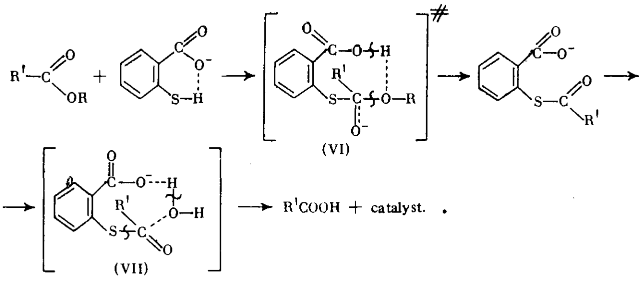
† For clarity, as in previous communications, the bond arising in transition states will be designated by dashed lines and the bond undergoing dissociation, by a crossed line.

The bifunctional mechanism of the catalysis of the hydrolysis of esters by *NN*-dialkylhistamine[48] [scheme (8)], incompletely ionised mercaptobenzoic acid[49] [scheme (9)] or catechol[50], etc. (see, for example Schatzle et al.,[51] Yakovlev and Rozengart[52], and Bender[1], pp.104–115) has been fully demonstrated:



(8)

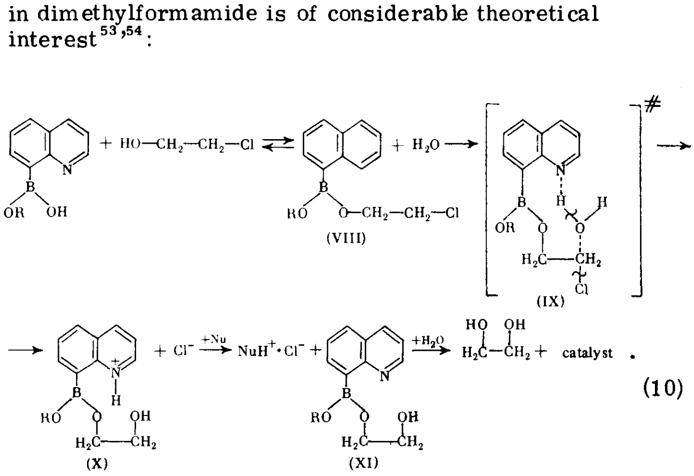


(9)

According to scheme (8) polyfunctional imidazole derivatives such as *NN*-dialkylhistamines, which are more active than imidazole itself by 1–1.5 orders of magnitude, initially add to the ester via their heteroaromatic ring, in such a way that the subsequent elimination of the outgoing group with the aid of the dialkylammonium centre in the side chain [transition state (IV)] is promoted; this results in the formation of an intermediate acylimidazole derivative. Since this amide does not differ greatly in its reactivity from that of the initial esters, it is natural to postulate catalysis by the dialkylamino-side group also in the subsequent hydrolytic stage [transition state (V)]. The anions of *o*-mercaptobenzoic acid [scheme (9)] and catechol behave similarly.

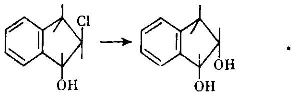
As regards the nature of their activity, the bifunctional catalysts considered resemble hydrolytic enzymes, which usually form covalently linked enzyme–substrate complexes with ester molecules.

The hydrolysis of chloroalcohols $Cl-(CH_2)_n-OH$ (where $n = 2$ or 3) in the presence of catalytic amounts of quinoline-8-boronic acid or its partial esters and collidine (Nu) in dimethylformamide is of considerable theoretical interest[53,54]:



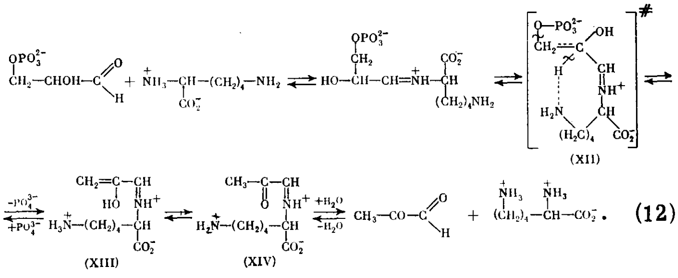
(10)

In this case quinoline-8-boronic acid accelerates the reaction approximately by an order of magnitude compared with the control experiment. It is of interest that quinoline-8-boronic acid exhibits a high stereospecificity in its activity, which may be demonstrated by the fact that, of the two possible stereoisomers of 2-chloro-1-indanol, only the *trans*-isomer undergoes catalytic hydrolysis. Under these conditions, the reaction proceeds with inversion of configuration, because only *cis*-1,2-indandiol is formed:



(11)

Certain elimination, enolisation, and isotope exchange reactions involving carbonyl compounds, catalysed by aminoacids and diamines, proceed with participation of covalently linked intermediates comprising the substrate and the catalyst. Thus lysine catalyses the conversion of 3-phosphoglyceraldehyde into pyruvic aldehyde[55] via the following mechanism:



(12)

According to scheme (12), a lysine molecule forms an immonium cation with the substrate via the 2-amino-group, which then decomposes with participation of the second amino-group via the cyclic transition complex (XII) and gives rise to the intermediate (XIII) and the latter hydrolyses and is converted into pyruvic aldehyde with regeneration of the catalyst.

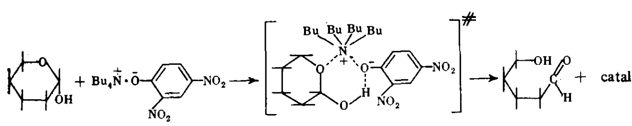
A similar mechanism of catalysis apparently obtains also in the exchange of deuterium in acetone-d_6 for hydrogen in an aqueous solution in the presence of diamines of the type $(CH_3)_2N-(CH_2)_n-NH_2$ (where n = 2, 3, 4, or 5) and polyethylene-imines[56], which are more effective approximately by an order of magnitude than the monoamines having similar pK_a values. As regards the nature of their action, the above diamine catalysts resemble the so called pyridoxal enzymes, in the presence of which pyridoxal phosphate forms with the substrate a Schiff base, which then undergoes various rearrangements (see, for example, Poltrak and Chukhrai[57] and Jencks[2], p.112).

Whereas tautomeric catalysts must contain two functional groups with opposite properties (nucleophilic and electrophilic), which undergo interconversions, this requirement is not obligatory for covalent catalysts. They therefore include substances containing functional groups of different types (nucleophilic and electrophilic—quinoline-8-boronic acid, monoanions of mercaptobenzoic acid and catechol, etc.) as well as groups of the same type (both nucleophilic—diamines and amino-acid anions).

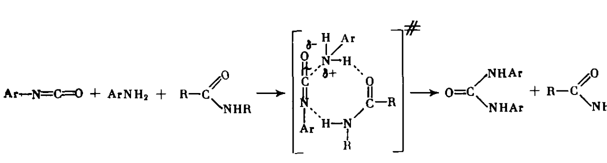
Yet another characteristic feature of covalent catalysts emerges from the foregoing considerations. Reactions with their participation must always involve intermediate stages with intramolecular catalytic action leading to the formation of cyclic transition states.

3. Bifunctional Solvation Catalysts

In a general form the mechanism of the action of solvation catalysts can be represented by scheme (2), but, in contrast to tautomeric catalysts, they are not directly involved in bond redistribution. Nor do these catalysts form covalent bonds with the reactants. Solvation catalysts activate via cyclic transitions states of type (I) certain sections of the reactants, either as a result of the formation of hydrogen bonds or as a result of electrostatic, dispersion, and other forces. Consequently, the nature of the forces in the interaction of a bifunctional solvation catalyst with reactants is the same as in specific and nonspecific solvation. As an example of catalytic reactions of this type, one may quote the catalysis by ion pairs formed from 2,4-dinitrophenoxide and tetra-alkylammonium of the mutarotation of TMG in benzene[16] [scheme (13)], the catalysis by amides of the reactions of phenyl isocyanate with amines[58] [scheme (14)], and the analogous reactions of ketens with alcohols[59]:



(13)



(14)

It follows from experimental data[58,59] that the above catalysts are less effective in reactions (13) and (14) by approximately 1–2 orders of magnitude than tautomeric catalysts such as carboxylic acids.

The acceleration of the solvolysis of t-butyl bromide[60] and the decarboxylation of malonic acid[61] by dihydric phenols and alcohols, which are appreciably more effective than the corresponding monofunctional analogues, may be apparently also regarded as solvation catalysis.

III. QUANTITATIVE FEATURES OF REACTION KINETICS

Analysis of all the available results shows that, among the three classes of catalysts discussed above, bifunctional tautomeric catalysts exhibit the greatest efficiency, because they promote bond redistribution as a result of the simultaneous transfer of two protons via the cyclic system without any appreciable charge separation. Since catalysts of this class have been most thoroughly investigated, we shall consider further the main characteristics of the action of tautomeric catalysts. The data quoted below will probably prove useful also in understanding the properties of other classes of polyfunctional catalysts.

1. The Influence of the Structure of Bifunctional Tautomeric Catalysts on Their Activity

The influence of the structure of bifunctional catalysts on their activity has been most thoroughly studied in relation to the acylation of arylamines by carboxylic acid halides and anhydrides[62–68], the aminolysis of esters[11,69], peptide formation[39,40,70], and the mutarotation of tetramethylglucose[7,9,10–13,15] in non-polar aprotic media. In the above studies the catalytic rate constants k_m were determined quantitatively on the basis of the following general relation between the observed rate constant k_{obs} and the analytical catalyst concentration m:

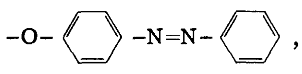
$$k_{\text{нб}} = k_0 + k_m m\alpha, \tag{15}$$

where k_0 is the non-catalytic rate constant, α the degree of dissociation of the catalyst dimers into monomers, and $m\alpha$ the concentration of the monomeric form of the catalyst. Eqn. (15) reflects quantitatively the fact, noted above, that only the monomeric form of the catalyst exhibits catalytic activity‡.

Table 1. The efficiencies of certain monofunctional and bifunctional catalysts in acylation and peptide formation* reactions (in benzene at 25°C).

No.	Catalyst	k_m, (1), litre^2 mole^{-2} s^{-1}	k_m/k_0, (1), litre mole^{-1}	k_m, (2), litre^2 mole^{-2} s^{-1}	k_m/k_0, (2), litre mole^{-1}
1	Acetic acid	0.450	132 000	280	2 900 000
2	2-Hydroxypyridine	10**[72]	28 500	5,6	60 000
3	5-Bromo-2-hydroxypyridine	0.112	83 000	33,0***	165 000
4	*N*-Methyl-2-pyridine	0	0	0	0
5	2-Methoxypyridine	0	0	—	—
6	Pyridine	0	0	0	0
7	3,4-Dinitrophenol	0**[73]	0	—	—
8	3-Hydroxypyridine	0	0	—	—

* (1) acylation reaction: C_6H_5COF + m-$ClC_6H_4NH_2$, k_0 = 3.4×10^{-6} litre mole^{-1} s^{-1};[71] (2) peptide formation reaction: Z-gly-OPAP + t-BEG, k_0 = 9.6×10^{-5} litre mole^{-1} s^{-1},[70] where Z-gly = $C_6H_5CH_2OCONHCH_2CO$–, OPAP =



, and t-BEG = t-butyl ester of glycine.

** For the interaction with *p*-anisidine.

*** Reaction in chlorobenzene.

The bifunctional nature of the catalysis in the above instances has been demonstrated in relation to a large number of examples. Swain's evidence[7] in support of the bifunctional activity of 2-hydroxypyridine in mutarotation has already been mentioned. Table 1 presents data indicating the occurrence of bifunctional catalysis by carboxylic acids, 2-hydroxypyridine, and its derivatives in the peptide formation reaction and in the acylation of amines by an acid halide in benzene§. Thus 2-hydroxypyridine and its 5-bromo-derivative (Table 1, Nos. 2 and 3) are powerful catalysts both in the peptide formation reaction and in the

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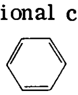
‡ In certain cases (mutarotation of TMG[10,12], acylation of strong amines[63], and peptide formation[39,40]) a correction must be introduced into Eqn. (15) for the formation of inactive associated species comprising the catalyst and the reactants (see also below).

§ Here and henceforth the catalytic activity of a particular catalyst is estimated as the ratio k_m/k_0. This quantity is extremely convenient for comparing the efficiencies of organic catalysts, exhibiting their activity in a wide variety of reactions under a wide variety of conditions.

acylation of arylamines by benzoyl fluoride, while 3-hydroxypyridine (Table 1, No. 8) and other monofunctional substances, containing only one acid or basic group, exhibit no activity (Table 1, Nos. 4–7). Acetic acid (Table 1, No. 1) exhibits a very high activity, while 3,4-dinitrophenol, which has a comparable acid strength (Table 1, No. 7, a monofunctional acid), as well as a base such as pyridine (Table 1, No. 6) show no catalytic activity whatever in the instance under consideration.

The data in Table 2 indicate the bifunctional nature of the catalysis by pyrazole in peptide formation. Indeed both phenol and *N*-methylpyrazole hardly catalyse the above reaction, while pyrazole itself is fairly effective. It is of interest that a pair of compounds such as imidazole and its *N*-methyl derivative exhibit low and approximately the same catalytic activities. Taking this factor into account as well as the fact that the disposition of the functional centres in imidazole is unfavourable for bifunctional catalysis and the considerable basicity of the latter pair of compounds (Table 2), we suggest that the usual base catalysis operates in this instance.

Table 2. The efficiencies of pyrazole, imidazole, and certain monofunctional compounds in the reaction of Z-gly-ONP (ONP = –O–  –NO_2) with t-BEG (in benzene at 25° C; $k_0 = 5.7 \times 10^{-4}$ litre $mole^{-1}$ s^{-1} [74]).

Catalyst	k_m, $litre^2$ $mole^{-2}$ s^{-1}	k_m/k_0, litre $mole^{-1}$	pK_a[77] (Ref.77)
Pyrazole (Ref.75)	1.74	3000	2.47
N-Methylpyrazole (Ref.75)	0.01	17	2.04
Phenol (Ref.85)	0	0	
Imidazole (Ref.76)	<0.49	<850	6.95
N-Methylimidazole (Ref.76)	0.49	850	7.33

The bifunctional mechanism of the catalysis by carboxylic acid and 2-hydroxypyridine derivatives is described by the general scheme (6). The mechanism of the catalysis by pyrazole can be represented by an analogous scheme[75].

Table 3 as well as other data (see, for example, Rony[11,12]) show that, among all the bifunctional catalysts investigated in a wide variety of different types of reaction, the highest catalytic activity is shown by carboxylic acids, phosphinic acids, and 2-hydroxypyridine.

An attempt was made[12] to investigate the catalytic activity of strong bifunctional acids such as benzenearsenic, benzenesulphonic, benzenesulphinic, etc. acids, in the mutarotation of TMG in non-polar media. Owing to experimental difficulties, it was not possible to calculate the values of k_m for the above substances. However, qualitative comparisons with other bifunctional catalysts showed that the strong acids have efficiencies comparable to those of phosphinic acids of the type R_2POOH, where R may be alkyl, aryl, and aryloxy-groups.

Depending on the nature of the reaction investigated, the relative activities of phosphinic acids, carboxylic acids, and 2-hydroxypyridine may vary. Thus carboxylic acids are most active in peptide formation, being followed in this respect by 2-hydroxypyridine and phosphinic acids (Table 3). In the mutarotation of TMG and in the acylation of arylamines by acetic anhydride phosphinic acids are the most effective and are followed in this respect by carboxylic acids and then 2-hydroxypyridine (Table 3, Nos. 1–8). The change in the order of the catalytic activities of bifunctional catalysts as a function of the nature of the model reaction may have a number of causes. We shall consider one of these.

Table 3. The efficiencies of bifunctional tautomeric catalysts (k_m/k_0, litre $mole^{-1}$) in various reactions in benzene and chlorobenzene at 25° C.

No.	Catalyst	Reaction* (1)	(2)	(3)	(4)	(5)
1	CH_3COOH	40 000**	300^{80}	$1\,200^{78}$	$1\,200\,000^{40}$	—
2	CCl_3COOH	720 000**	4800^{63}	—	—	—
3	C_6H_5COOH	660 000	1200^{80}	—	—	—
4	2-Hydroxypyridine	160 000	1700^{71}	—	—	30 000
5	$(C_6H_5)HPOOH$	140 000 000	—	—	—	—
6	$(C_6H_5)_2POOH$	—	—	$105\,000^{67}$	$14\,000^{79}$	—
7	$(C_4H_9)_2POOH$	—	400^{68}	$7\,200^{67}$	$30\,000^{79}$	—
8	$(C_6H_5O)_2POOH$	430 000 000	—	—	$4\,300^{79}$	—
9	Pyrazole	910	—	—	$3\,000^{75}$	—
10	2-Aminopyridine	3 900	—	—	—	320
11	8-Hydroxyquinoline	—	—	—	—	0
12	Picric acid	920	—	—	—	—

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*Reactions: (1) mutarotation of TMG[12], $k_0 = 0.65 \times 10^{-5}$; (2) $C_6H_5COCl + m\text{-}ClC_6H_4NH_2$, $k_0 = 3.3 \times 10^{-3}$; (3) $(CH_3CO)_2O + m\text{-}ClC_6H_4NH_2$, $k_0 = 7.6 \times 10^{-4}$; (4) Z-gly–ONP + t-BEG, $k_0 = 5.7 \times 10^{-4}$; (5) Z-gly–OPAP + t-BEG, $k_0 = 2.0 \times 10^{-4}$ litre $mole^{-1}$ s^{-1}; reactions (1)–(4) were carried out in benzene and reaction (5) in chlorobenzene.
**Values taken from Kergomard and Renard[15], where, in contrast to Rony and Neff[12], no account was taken of the association of the catalyst with TMG, which decreases k_{obs}.

When arylamines are acylated by acid anhydrides and chlorides, bifunctional catalysts more acidic than acetic and benzoic acids (for example trichloroacetic acid) exhibit, together with the catalytic effect observed at low catalyst concentrations, also an inhibitory activity[63] as the catalyst concentration rises (see Fig. 1). This can be accounted for by the interaction of the catalyst with the amine, leading to the formation of an unreactive salt:

$$R{-}COOH + R{-}NH_2 \rightleftarrows RCOO^- \cdot \overset{+}{N}H_3R\ (XVII). \qquad (16)$$

Salt formation interferes with catalysis even more in the aminolysis of esters by aliphatic amines[81] and in peptide formation reactions[39,40]. In these reactions even acetic acid, which in this instance exhibits the highest activity, is catalytically active only at low concentrations (up to 0.01 M). At higher concentrations inhibition takes place. It is extremely likely that this is the reason as already mentioned, why the stronger phosphinic acids exhibit a much smaller catalytic effect in the peptide formation reaction than carboxylic acids and 2-hydroxypyridine.

The high catalytic activity of tautomeric catalysts has also been confirmed by the quantum-chemical calculations carried out by Gold[13] using the Hückel method: in the calculations account was taken of the fact that during the catalytic step, a π-electron distribution, analogous to that demonstrated in scheme (5), takes place in the catalyst. The interaction indices ξ calculated for these conditions constitute a linear combination of general perturbations in the functional groups of the catalyst during the formation of the cyclic transition state (II) and characterise the energy gain as a result of such electron distribution. The values of ξ for a number of catalysts are presented in Table 4. The indices reflect the capacity of the bifunctional catalyst for a tautomeric transformation in the course of the catalytic reaction. It follows from the data in Table 4 that there is a linear correlation between the values of $\lg k_{\text{obs}}$ (calculated for constant TMG and catalyst concentrations) and the interaction index ξ.[13] This suggests that the following linear relation should exist in its turn, other conditions being equal, between the catalytic activity of a bifunctional catalyst and the rate of conversion of its tautomeric form involved in the catalytic step into another form (the relation follows from the principle of the linear relation between the free energy changes):

$$\lg k_m = a + b \lg k_{\text{taut}}, \tag{17}$$

where k_{taut} is the rate constant for the tautomeric transformation. In this theoretical treatment the simplest case is one where both tautomeric forms are identical (carboxylic, phosphinic, sulphonic, etc. acids, pyrazole). Under these conditions, the catalyst is immediately regenerated in the course of the catalytic step. The constant k_{taut} is in this instant in essence the rate constant for proton exchange involving the catalyst dimers. The rate of the process can then increase only up to a limiting value determined by the rate of diffusion of the species in solution. Under these conditions, the catalytic activity of the bifunctional catalyst evidently also reaches the maximum possible value for a simple functional structure. Catalysis by diphenyl phosphate (Table 3, No. 8), which accelerates the mutarotation of TMG in benzene by approximately nine orders of magnitude, apparently approaches this limiting case. Such activity is comparable to that of enzymes (the lower limit of the acceleration of the reaction by the latter is by 9–11 orders of magnitude; see Jencks[2], p. 23).

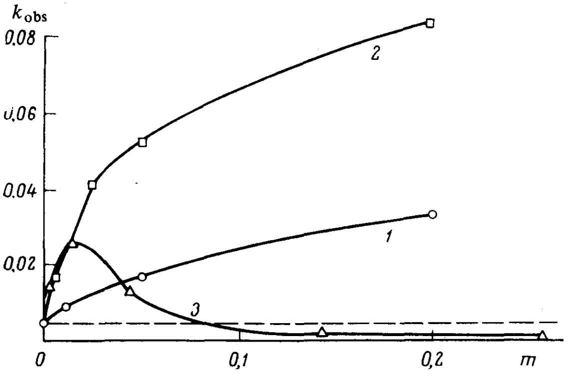
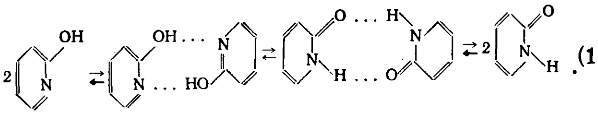


Figure 1. Dependence of the observed rate constant for the benzoylation of *m*-chloroaniline by benzoyl chloride on the analytical concentration (*m*) of carboxylic acids in benzene[63] at 25°C: 1) acetic acid; 2) monochloroacetic acid; 3) trichloroacetic acid.

The situation is more complex for bifunctional catalysts whose tautomeric forms are structurally non-equivalent. An example is provided by 2-hydroxypyridine, the two tautomeric forms of which are different and the equilibrium between them is determined by the solvent[82]:

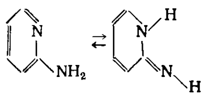

(18)

In conformity with the above considerations, the form which is more readily converted into the other tautomer, i.e. the less stable form present at a lower equilibrium concentration, should exhibit a higher catalytic activity. Or, what amounts to the same thing, the more stable form should exhibit a low catalytic activity. This conclusion is entirely logical and is indirectly confirmed by the examples quoted below.

Table 4. Comparison of experimental data for the catalytic activities of bifunctional catalysts in the mutarotation of TMG in benzene with the interaction indices ξ.[13]

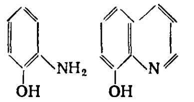
Catalyst	k_{obs}, s^{-1}	ξ
Benzoic acid	0,0636	0.206
2-Hydroxypyridine	0.0163	0.0806
2-Hydroxy-4-methylquinoline	0.00638	0,0789
2-Aminopyridine	0.002	0,0230
Picric acid	0.00076	0

Substances for which tautomeric transformations are relatively unlikely show a lower catalytic activity or are altogether inactive. Thus 2-aminopyridine (Tables 3 and 4), which exists in the stable amino-form[83] (XVIII) whose conversion into the imino-form (XIX) via reaction (19) hardly occurs, behaves as a relatively ineffective catalyst in the mutarotation of TMG:

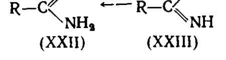

(XVIII) (XIX)

(19)

As already mentioned, 2-hydroxypyridine is an active catalyst of the peptide formation reaction and 2-aminophenol (XX)[11] and 8-hydroxyquinoline (XXI) (Table 3), which are incapable of undergoing a tautomeric transformation, are catalytically altogether ineffective:


(XX) (XXI)

Evidently carboxylic acid amides, for which form (XXIII) is thermodynamically unfavourable[84] and is not detected in a free state, do not exhibit bifunctional catalytic activity for the same reasons:


(XXII) (XXIII)

$$\mathrm{R{-}C}\genfrac{}{}{0pt}{}{\nearrow \mathrm{O}}{\searrow \mathrm{NH_2}} \;\rightleftarrows\; \mathrm{R{-}C}\genfrac{}{}{0pt}{}{\nearrow \mathrm{OH}}{\searrow \mathrm{NH}} \tag{20}$$

The absence of bifunctional activity in amides containing a hydrogen atom attached to the nitrogen atom has been frequently demonstrated[37,85] in relation to the acylation of arylamines by carboxylic acid halides and certain other related reactions.

Thus the bifunctional catalysis by the same amides in reactions involving phenyl isocyanates[58] and ketens[59] (see also the above discussion of solvation catalysts) must be assumed to have a solvation and not a tautomeric mechanism.

2. The Dependence of the Activities of Bifunctional Catalysts on Their Ability to Form Hydrogen Bonds

Yet another necessary condition for the manifestation of bifunctional catalytic activity is a distinct ability of the catalyst to form hydrogen bonds. This can be demonstrated in relation to catalysis by acetic acid and its thio-analogues of the acylation of arylamines by acetic anhydride and benzoyl chloride in benzene, and also in the mutarotation of TMG (Table 5). In the above experiments the structure of the reactant remained unchanged and only the nature of the catalyst was varied in such a way that it acquired different capacities for the formation of hydrogen bonds. Indeed, the catalytic activity of the acid fell sharply as the oxygen atoms were replaced by sulphur, although its strength increased significantly at the same time.

Table 5. The values of k_m (litre^2 mole^{-2} s^{-1}) and k_m/k_0 (litre mole^{-1}) for the reactions of benzoyl chloride and acetic anhydride with *m*-chloroaniline catalysed by acetic acid and its thio-analogues[80] and for the mutarotation of TMG[15] (in benzene at 25°C).

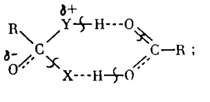
Catalyst	$C_6H_5COCl+ArNH_2$		$(CH_3CO)_2O+ArNH_2$		Mutarotation of TMG	
	k_m	k_m/k_0	k_m	k_m/k_0	k_m	k_m/k_0
CH_3—CO—OH	1.01	300	6.98	6200	0.26	40 000
CH_3—CO—SH	0.03	9	—	—	0.007	1 100
C_6H_5—CO—SH	0.03	9	0.47	400	—	—
CH_3—CS—SH	0	0	0	0	—	—

The main cause (although evidently not the only one) of the decrease of the efficiency of catalysis in the above series of catalysts is the reduced ability of the SH group to form hydrogen bonds[86,87], which hinders the combination of the participants in the catalytic step into cyclic transition states of type (II) or (III). Indeed, on passing from carboxylic acids to their thio-analogues, the capacity for association diminishes sharply. For example, thioacetic and thiobenzoic acids, which are relatively ineffective in catalysis, are not associated even in the liquid state[88]. However, dithioacetic acid, which exhibits no activity, is in fact capable of association (being significantly inferior in this respect to carboxylic acids), since it exists partly in the dimeric form in the liquid state; infrared spectra also indicate the presence of comparatively strong hydrogen bonds in this acid[88]. Thus the above catalysts can be arranged in the following sequences in terms of their catalytic activities and abilities to form hydrogen bonds:

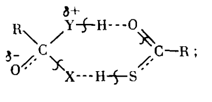
R—COOH ≫ R—COSH > R—CSSH (catalytic activity);

R—COOH ≫ R—CSSH > R—COSH (ability to form hydrogen bonds).

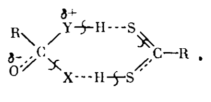
The lack of a parallel variation of these two properties can apparently be explained by the fact that the formation of a hydrogen bond is a necessary but not sufficient condition for the manifestation of catalytic activity, because, as stated in the previous section, the ability of the catalyst to undergo a tautomeric transformation or, what amounts to the same thing, to transfer a proton via hydrogen bonds in the cyclic transition state, is more important. The rate of proton transfer is known to decrease in the following sequence: OH ... O > OH ... N > SH ... O > SH ... N > SH ... S.[89-91]. In catalysis by acetic acid rapid proton transfer may be ensured by both hydrogen bonds [see, for example, compound (XXIV)]; in the analogous reaction involving thioacetic acid [transition state (XXV)], only one of the two bonds effects proton transfer (the overall transfer is retarded), while in the presence of dithioacetic acid [transition state (XXVI)] there is no hydrogen bond of this kind, although, as already mentioned, each separately can in principle be somewhat stronger than the bond involving the SH group of thioacetic acid.



(XXIV)



(XXV)



(XXVI)

The important role of the hydrogen bond in bifunctional tautomeric catalysis has also been confirmed by theoretical calculations[14] (within the framework of the LCAO-MO SCF method in terms of the CNDO/2 valence approximation), carried out for the mutarotation of glucose catalysed by 2-hydroxypyridine. The calculations showed that the two hydrogen bonds in the cyclic glucose–2-hydroxypyridine complex are stronger than the two isolated bonds and initiate the rearrangement of the electron cloud of the substrate and catalyst during the catalytic step.

Thus the hydrogen bond is the factor which ensures the optimum mutual approach and relative arrangement of the bifunctional catalyst and the reactant, i.e. one may assume that in tautomeric bifunctional catalysis the catalytic reaction must be always preceded by the preliminary formation of cyclic associated species via hydrogen bonding between the reactants and the catalyst. The existence of such species is very difficult to demonstrate experimentally because, by their very nature, they must be naturally extremely unstable. However, their existence is indicated by the formation during the reactions of stable associated species stimulated by the bifunctional catalyst: the cyclic dimers of bifunctional catalysts[10,15,46,47] and associated species formed from the catalyst and one of the reactants. The presence of the latter has been noted, for example, in the catalytic acylation of amines[63], peptide formation[39,40], or the mutarotation of TMG[10]. Such associated species decrease the concentration of the active form of the catalyst and of the reactants, which is manifested by kinetic factors (see, for example, Refs. 10, 15, 39, 40, 46, 47, and 63).

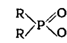
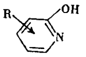
3. The Influence of Substituents in Bifunctional Tautomeric Catalysts on Their Activity

In many instances the influence of substituents in bifunctional catalysts (carboxylic and phosphinic acids and substituted derivatives of 2-hydroxypyridine, see Table 6) has been estimated by correlation analysis. The Taft or Hammett equation was used:

$$\lg k_m = \lg k_{m(\text{ст})} + \rho^*\sigma^* \text{ (or } \rho\sigma). \tag{21}$$

It follows from the data in Table 6 that the introduction of electron-accepting substituents, which tend to increase the acid strength of the electrophilic part of the catalyst molecule and at the same time diminish the basic properties of the nucleophilic component, leads to increased activity of the catalyst in the vast majority of reactions investigated (with the exception of catalysis by carboxylic acids in dioxan and by phosphinic acids in benzene for reaction No. 9 in Table 6). The positive sign of $\rho^*(\rho)$ shows that the acid function of the catalyst plays the main role in the catalytic action.

Table 6. The values of $\rho^*(\rho)$ characterising the influence of substituents in a bifunctional catalyst on its catalytic activity* (values calculated from literature data are indicated in brackets; the solvents are indicated by capital letters, also in brackets, next to the numerals: B = benzene; N = nitrobenzene; C = chlorobenzene; D = dioxan).

No. of reaction	Catalyst	RCOOH		
		t-C_4H_9, CH_3, C_6H_5, CH_2Cl, CCl_3 etc .	C_4H_9, C_6H_5, C_6H_5O	H, 5-CH_3, 4-CH_3, 5-Cl, 5-Br
1	$C_6H_5COF + p\text{-}CH_3O{-}C_6H_4NH_2$	—	—	$(+1.8)(B)^{71}$
2	$C_6H_5COCl + m\text{-}Cl{-}C_6H_4NH_2$	+0.41 (B) (Ref.66)	—	$(\sim 0)\ (B)^{71}$
3	$C_6H_5COCl + m\text{-}NO_2{-}C_6H_4NH_2$	+0.13 (N) (Ref.66)	—	—
4	$(CH_3CO)_2O + m\text{-}Cl{-}C_6H_4NH_2$	+0.68 (B) (Ref.66)	$+0.79\ (B)^{67}$	—
5	$(CH_3CO)_2O + m\text{-}NO_2{-}C_6H_4NH_2$	+0.56 (N) (Ref.66)	—	—
6	$(CH_3CO)_2O + p\text{-}NO_2{-}C_6H_4NH_2$	+0.72 (B) (Ref.66)	—	—
7	$CH_3CO{-}OC_6H_3(NO_2)_2 +$ $+ C_6H_5NH_2$	+0.18 (B) (Ref.69) +0.14 (D) (Ref.69)	—	—
8	Z-gly-OPAP + t-BEG	—	—	$(+2.4)\ (X)^{70}$
9	 + t-BEG	$+0.24\ (B)^{40}$** $(-0.18)\ (D)^{39}$***	$-0.25\ (B)^{79}$**	—
10	Mutarotation of TMG	$(+0.50(B)^{15}$	—	—

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*The values of ρ are approximate, because it is not known which value should be adopted for substituents in the 5-position: σ_m or σ_p.

**R = H.

***R = $C_6H_5CH_2$–.

The low absolute values of ρ^* (ρ), sometimes approaching zero, usually constitute an additional confirmation of the bifunctional nature of the catalysis, because the increase of the strength of the acid function in the catalyst molecule should stabilise the cyclic structure of the transition state and the weakening of the nucleophilic function should play a destabilising role to approximately the same extent.

The compensation effect is manifested particularly clearly in catalysis by carboxylic and phosphinic acid in the aminolysis of esters and in peptide formation (see reactions Nos. 7 and 9, Table 6). The low value of ρ^* in the above instances can be accounted for by the fact that acylating agents with outgoing groups which are difficult to eliminate take part in these reactions (ArO is split off with greater difficulty than Cl, RCO–O, etc.[92]); in the elimination of these groups the abstraction of a proton from the attacking amine assumes great importance[93] and the role of the basic function of the bifunctional catalyst increases. The latter leads to more complete compensation of the effect of the acid and basic functions. The suggested enhancement of the role of proton abstraction from the attacking amine in the rate-determining stage with decrease in the tendency of the outgoing group to be eliminated is supported by the increased efficiency of base catalysis on passing from reactions involving acid anhydrides and halides, where there is no base catalysis[94], to the aminolysis of esters where the catalytic process involving a base-catalytic mechanism predominates over the non-catalytic process[93]. The role of the basic catalyst in the latter reactions reduces to the elimination of a proton from the attacking amine.

The negative values of ρ^* in the catalysis of the peptide formation reaction by carboxylic acids in dioxan and by phosphinic acids in benzene (Table 6, No. 9) may indicate that in this instance the basic function of the bifunctional catalyst predominates over the acid function in the catalytic step.

4. The Influence of the Nature of the Reactants on the Activity of Bifunctional Catalysts

It follows from the data in Table 3 that a change in the structure of the reactants has a very significant influence on the catalytic activity of bifunctional catalysts. We shall consider a few more examples. Suppose that the outgoing group X in the acylating agent consists of various halogen atoms (ranging from F to I), the nature of which determines to a significant extent the strength of the hydrogen bonds involving them. It follows from the data in Table 7 that in the case of the fluoro-derivative, which exhibits a particularly striking ability to form a hydrogen bond, acetic acid has an exceptionally high catalytic activity (see the values of k_m/k_0), which falls sharply on passing to reactions involving the remaining acid halides. It has been shown[96] that under these conditions there is a linear correlation between the activity of the catalyst and the capacity of the outgoing group (the halogen) for the formation of a hydrogen bond. The increase of the ability of the halogen to form a hydrogen bond facilitates, as already mentioned, the formation of cyclic transition states of type III and hence promotes the catalytic processes.

The high activity of acetic acid in the reaction involving anhydrides (Table 7) can also be explained by the fact that the anhydride oxygen atom is able to form strong hydrogen bonds.

Table 8 shows that the catalytic activity of acetic acid increases on passing from the reaction of *p*-nitrophenyl thioacetate with benzylamine to the corresponding reaction of *p*-nitrophenyl acetate, which is also consistent with all the foregoing considerations. In this connection one should also mention that in the series of thioesters the catalytic activity of acetic acid increases with enhancement of the electrondonating properties of the outgoing thiophenoxide group ArS. In the latter case the cyclic transition complex is formed via ring closure involving a hydrogen bond of the type $>$S...H–O–. This type of hydrogen bond can be fairly stable[97], while the opposite type $>$O...H–S is always very weak. This is why carboxylic acids catalyse the aminolysis of thioesters, while thiocarboxylic acids are almost ineffective in the reactions of acid anhydrides and halides.

Thus the experimental study of the influence of the structure of the reactants on the catalytic activity of the same bifunctional catalyst has confirmed the great importance of the formation of strong hydrogen bonds in cyclic transition states.

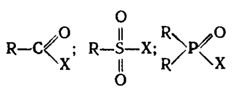
Table 7. Catalytic activity of acetic acid in the aminolysis of carboxylic acid halides[95] and anhydrides[78] (in benzene at 25° C).

Reaction	k_0, litre mole^{-1} s^{-1}	k_m, litre^2 mole^{-2} s^{-1}	k_m/k_0, litre mole^{-1}
$C_6H_5COHal+$*p*-anisidine			
for Hal=F	0.000225	66.1	294 000
Hal=Cl	1.21	171	141
Hal=Br	81.6	3250	40
Hal=I	192	7150	37
$(CH_3CO)_2O+$aniline	0.00470	110	23 000

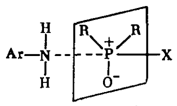
Table 8. The catalytic activity of acetic acid in the reaction of phenyl thioacetate and phenyl acetate derivatives with benzylamine[81] (in benzene at 25° C).

R	10^5k_0, litre mole^{-1} s^{-1}	k_m, litre^2 mole^{-2} s^{-1}	k_m/k_0, litre mole^{-1}
	$CH_3—CO—S—C_6H_4R$		
2.4-$(NO_2)_2$	113 000	0	0
o-NO_2	1 630	145	9 000
p-NO_2	101	99	100 000
m-Cl	1.3	12	900 000
H	0.15	6.5	4 000 000
	$CH_3—CO—O—C_6H_4R$		
2.4-$(NO_2)_2$	59 000	0	0
p-NO_2	29	25	800 000

From the standpoint of the influence of the structure of the reactant on the catalytic activity, the problem of the efficiency of the same bifunctional catalyst (for example, a carboxylic acid) in the aminolysis of acylating agents differing in the nature of the electrophilic centre is of interest. Comparison of data for catalytic nucleophilic substitution reactions at unsaturated carbon, sulphur, and phosphorus atoms in the compounds



showed that bifunctional catalysis by the acids RCOOH is clearly manifested only in the first instance[98]. This finding can be accounted for by the fact that the reaction involving substitution at a carbonyl carbon atom proceeds via the formation of transition states or intermediates [see scheme (6)] in which the constituent fragment of the bifunctional catalyst is complementary to the fragment formed from the reactants. Thus in the stereochemical sense a catalytic reaction involving substitution at the carbonyl carbon atom is entirely feasible. On the other hand reactions in which substitution is carried out at sulphur and phosphorus atoms proceed via transition states (intermediates) with the bipyramidal structure (XXVII):



(XXVII)

where the nucleophilic and electrophilic centres, which might be attacked by the bifunctional catalyst, are in the axial positions, i.e. are separated to the maximum possible extent. Cyclic transition complexes in the above two instances cannot therefore be achieved for stereochemical reasons.

The above examples show yet again how important is not only the nature of the functional centres in bifunctional catalysts and reactants but also their favourable disposition, necessary for the formation of a cyclic transition complex.

Table 9. The influence of substituents in the acylating agent and the primary arylamine on the catalytic activity of acetic acid characterised by k_m/k_0 (litre mole^{-1}) (in benzene at 25° C).

R	Reaction			
	C_6H_5COCl+ $+R—C_6H_4NH_2$[99]	$(CH_3CO)_2O+$ $+R—C_6H_4NH_2$[78]	$(CH_3CO)_2S+$ $+R—C_6H_4NH_2$[100]	*m*-$Cl—C_6H_4—$ $—NH_2+R—$ $—C_6—H_4COCl$[101]
m-CH_3O	—	—	—	215
H	193	23 000	16 000	306
p-Cl	273	—	—	—
m-Cl	300	12 000	13 000	—
m-NO_2	—	6 700	15 000	487
p-NO_2	285	—	—	476

The influence of substituents in both reactants (Table 9) on the catalytic activity of acetic acid in aminolysis has been investigated in a number of studies. It has been found that substituents in the *m*- and *p*-positions, both in the acylated amine and in the acylating agent, have only a slight influence on the catalytic activity of the bifunctional catalyst. However, if the substituent is directly at the reaction centre, as, for example, in *N*-alkyl-*m*-nitroaniline, then its effect is manifested to a much greater extent. Data concerning the influence of *N*-alkyl substituents in *m*-$NO_2-C_6H_4-NHR$ on the catalytic activity of acetic acid in the reaction involving acetic anhydride in benzene at 25° C[102] are presented below:

R	10^3k_m, litre^2 mole^{-2} s^{-1}	k_m/k_0, litre mole^{-1}
H	850	6500
CH_3	28	540
C_2H_5	11	240
iso-C_3H_7	0.058	87

The data presented show that a gradual increase in the bulk of the substituent leads to a significant decrease of catalytic activity owing to the steric effect, while the role of the inductive effect is hardly significant under these conditions (cf. also in the data in Table 9). Consequently, N-alkyl groups in an aliphaticaromatic amine create steric hindrance to the formation of cyclic transition states, which reduces the activity of the bifunctional tautomeric catalyst.

5. The Influence of the Medium on the Activity of Bifunctional Catalysts

The problem of the influence of the medium on the activity of bifunctional catalysts has been investigated in many instances in relation to the reactions considered in this review. Analysis of the available results shows that, with increase of the polarity of a non-specific solvent, the reaction rate constants decrease in bifunctional catalysis. The quantitative dependence of the rates of catalytic reactions on the polar properties of the solvent is illustrated in Fig. 2, where the values of $\lg k_m$ are compared with the Kirkwood function. Line I refers to reactions involving the formation of a simple amide linkage in catalysis by acetic acid[78] and line II characterises the formation of a peptide bond catalysed by 2-hydroxypyridine[70]. The observed negative influence of the polarity of the medium agrees with the bifunctional mechanism of the catalysis. Indeed, as already mentioned, the small separation of the charges in the cyclic transition state of type III makes the polarity of the latter lower than that of the initial reactants. For this reason, polar solvents stabilise the initial state and hinder the formation of cyclic transition complexes, which reduces the rate.

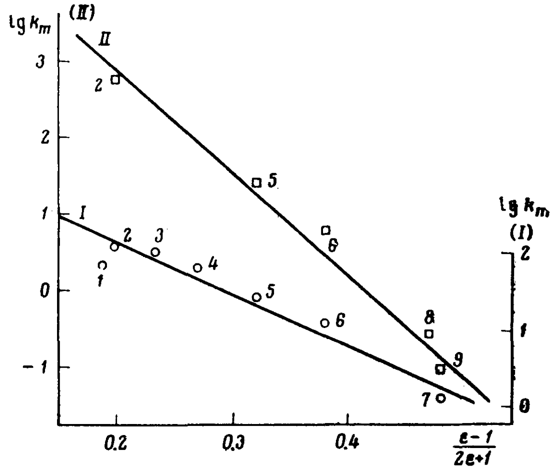


Figure 2. Dependence of $\lg k_m$ on $(\epsilon - 1)/(2\epsilon + 1)$ for the reaction of acetic anhydride with *m*-chloroaniline catalysed by acetic acid[78] (I) and for the reaction of the *p*-phenylazophenyl ester of *N*-benzyloxycarbonylglycine with *t*-butyl glycinate catalysed by 2-hydroxypyridine[70] (II) at 25° C; solvent: 1) hexane; 2) cyclohexane; 3)–5) cyclohexane–chlorobenzene mixtures with mole fractions of the latter of 0.106, 0.260, and 0.515 respectively; 6) chlorobenzene; 7) nitrobenzene; 8) benzonitrile; 9) acetonitrile. The values of $\lg k_m$ are plotted on the left-hand and right-hand ordinate axes for II and I respectively.

The results of a study of the catalytic activity of carboxylic acids in the reaction of 2,4-dinitrophenyl acetate with aniline in benzene and dioxan[69] at 25° C are presented below:

Catalyst	k_m/k_0, litre mole^{-1}	
	benzene	dioxan
$(CH_3)_3C—COOH$	11 000	5
$CH_3—COOH$	11 000	6
$ClCH_2—COOH$	19 000	10

The data presented (see also Rony[12]) show that the replacement of a non-specific solvent by a specific one (such as dioxan or alcohol¶), capable of forming strong hydrogen bonds with the reactants and the catalyst, also leads to a sharp decrease of catalytic activity because solvation by a specific solvent of the participants in the catalytic process and primarily of the catalyst itself, hinders the formation of cyclic transition states. Consequently the enhancement of the solvating capacity of the solvent (both specific and non-specific) leads to a decreased efficiency of bifunctional catalysis. Hence follows a conclusion which is important in practice: bifunctional catalysts are most effective in non-polar and weakly solvating media.

On the basis of the foregoing considerations, it is natural to expect that in water, which is a highly polar and specific solvent, bifunctional catalysis would be very difficult. For this reason, 2-hydroxypyridine behaves in aqueous solutions as an ordinary general basic catalyst, whose catalytic constant for the mutarotation of TMG falls on the usual Brønsted plot for basic substances with a slope $\beta = 0.37$.[12] Consequently the advantage of 2-hydroxypyridine as a bifunctional catalyst fully disappears in an aqueous medium. However, many reactions occurring in water are known in which bifunctional catalysis is nevertheless postulated. The carbonyl group is involved in one way or another in the above reactions; carboxylic acids, hydrogen phosphate anions, and dihydrogen phosphate anions may be used as bifunctional catalysts (in the hydrolysis of iminolactones[103], the addition of hydrogen peroxide to aldehydes[104], the hydration of aldehydes[105] and carbon dioxide[106], the hydrolysis of 1,3-diphenyl-2-imidazolium chloride[107], amides[108], acetimidate esters[109], etc.). One should note that the efficiency of bifunctional catalysts in water may be considerable[109].

Table 6 shows that, on passing from a non-polar solvent to a polar or specific solvent, the quantity ρ^*, characterising the sensitivity of the catalytic activity of the catalyst to the inductive influence of substituents in the latter (cf. reactions Nos. 2 and 3 and also 4, 5, and 6 in Table 6) decreases. The constant ρ^* sometimes changes sign under these conditions (reaction No. 9). In the latter case a specific solvent (dioxan) forms hydrogen bonds with the catalyst, reducing its acid function in the catalytic step[69], so that the basic function becomes dominant in catalysis (see also subsection 4 in this Section). Evidently, a similar function is fulfilled, albeit to a lesser extent, by non-specific solvents when their polarity is altered, which accounts for the decrease of ρ^* on passing from benzene to nitrobenzene.

IV. ENERGETIC PARAMETERS IN BIFUNCTIONAL CATALYSIS

The formation of cyclic transition states of type I is accompanied by a decrease of the energy barrier relative to processes proceeding via linear transition states

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¶Phosphinic acids in alcohol do not catalyse the peptide formation reaction in contrast to their solutions in benzene[79].

(Tables 10 and 11; see also Section I). One of the main causes of such decrease of the activation energy on formation of cyclic transition states is electron transfer via the ring, i.e. via a closed bond redistribution chain (BRC) (see Poltorak and Chukhrai[57], p. 264), which prevents any significant charge separation and hence decreases the associated energy barrier. In addition, Shilov[110] examined yet another cause of the decrease of the activation energy, consisting in the steric characteristics of the formation of the cyclic transition state, as a result of which preference must be given to cyclic rather than linear transition states (even in the absence of a closed BRC system in the former). In other words, the cyclic system fixes the reacting species in the positions most favourable for the chemical process (the Franck–Condon principle). Both these factors are apparently manifested in catalysis by bifunctional tautomeric catalysts, while in the case of bifunctional covalent and solvation catalysts, where there is no electron transfer via a ring (there is no BRC), only the second factor operates, as a result of which the last two classes of catalysts are appreciably inferior, as already mentioned, to the first as regards their efficiency.

In discussing the energetic parameters of bifunctional catalysis, account must be taken of the complexity of catalytic reactions, i.e. of the fact that they consist of many stages. Since the catalyst forms preliminary associated species with the reactants (see Section I), the catalytic rate constant may be represented as the product of at least two constants:

$$k_m = K^* k'_m, \qquad (22)$$

where K^* is the equilibrium constant for the formation of the preliminary associated species and k'_m the rate constant for the reaction with participation of this associated species. According to Eqn. (22), the observed activation energy E_a is defined by the equilibrium[111]

$$E_a = E'_{a(m)} - \bar{Q}_V\ , \qquad (23)$$

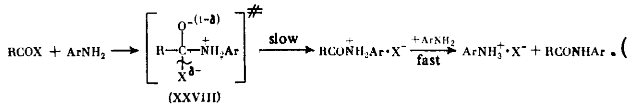
where $E'_{a(m)}$ is the activation energy for the stage characterised by the constant k'_m and $\bar{Q}_V$ the heat of formation of the preliminary associated species. Since $\bar{Q}_V > 0$, it follows that E_a is always less than the true value $E'_{a(m)}$. For this reason, the observed activation energies for catalytic reactions are negative in certain cases (see below), when $\bar{Q}_V > E'_{a(m)}$.

The energetic parameters were determined for the mutarotation of TMG (Table 10) and the acylation of arylamines by carboxylic acid chlorides, anhydrides, and esters (Table 11) stimulated by bifunctional catalysts. It follows from Table 10 that bifunctional catalysts of different types—2-hydroxypyridine and benzoic acid for the mutarotation of TMG—have virtually identical values of E_a and $\Delta S^{\#}$. On passing to basic monofunctional catalysts (pyridine and diethylamine), the values of E_a increase and those of $\Delta S^{\#}$ decrease. If the activation energies for catalysis by diethylamine and pyridine are extrapolated to the basicity of 2-hydroxypyridine, we obtain a value in excess of 20 kcal mole^{-1}. Consequently the activation energy for catalysis by 2-hydroxypyridine is lower by ~ 10 kcal mole^{-1} than the value predicted for general base catalysis. This corresponds to an increase of the rate of reaction by a factor of ~ 10^7. The increase of activation entropy on passing from basic to bifunctional catalysts is difficult to account for. For example, it has been suggested that this is associated with the change in the solvation shell of the transition complex (the freezing of the solvent in this shell)[12].

Whereas in the mutarotation of TMG the change from a monofunctional to a bifunctional catalyst leads to acceleration, mainly owing to the sharp decrease of the activation barrier, in the acylation reaction there is no such clear-cut behaviour. We may note that in acylation one may compare only the energetic parameters of the non-catalytic reaction (monofunctional catalysts are virtually ineffective) and the reaction stimulated by the bifunctional catalyst. Here it is possible to distinguish two groups of catalytic reaction.

1. Reactions to which correspond non-catalytic processes proceeding via non-cyclic transition states of type (XXVIII) [scheme (24)][100]. Reactions Nos. 1 and 3[100] and No. 5[112] belong to this class (Table 11).

2. Reactions to which correspond non-catalytic processes proceeding via cyclic transition states of type (XXX) or analogous states [scheme (25)][78,113]. These are reactions Nos. 2 and 4[100] and possibly Nos. 6[112] (Table 11):



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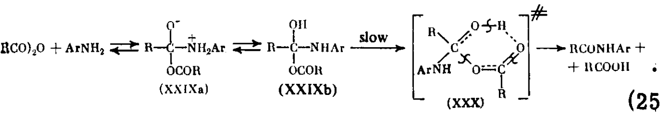

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Table 10. Energetic parameters for general base and bifunctional catalysis in the mutarotation of TMG in benzene[10,11].

Catalyst	E_a, kcal mole^{-1}	$-\Delta S^{\neq}$, e.u.	pK_a^{base} in H_2O
Benzoic acid	11.4	21.5	—
2-Hydroxypyridine	11.4	23.1	0.75
Diethylamine	14.3	26.3	10.98
Pyridine	>16.6	26.3	5.17

Table 11. Energetic parameters for non-catalytic (I) and carboxylic acid-catalysed (II) acylation of $C_6H_5NH_2$ in benzene (the catalyst was C_6H_5COOH in reaction Nos. 1 and 4 and CH_3COOH in all others).

No. of reaction	Acylating agent	E_a, kcal mole^{-1}	$-\Delta S^{\neq}$, e.u.	E_a, kcal mole^{-1}	$-\Delta S^{\neq}$, e.u.
		I		II	
1	C_6H_5COCl[100]	7.7	40.2	1.4	49.8
2	$(CH_3CO)_2O$[78]	0	71.7	0,9	48,2
3	$(CH_3CO)_2S$[100]	8.7	38.3	−1.8	54,2
4	$(C_6H_5CO)_2O$[100]	5.7	56.5	1.9	51.2
5	$CH_3CO{-}SC_6H_3(NO_2)_2$[112]	13.1	38.4	2.4	54.7
6	$CH_3CO{-}SC_6H_5$[112]	5.7	72.2	5.6	50.7

On passing from a non-catalytic to a catalytic process, both the activation energy and activation entropy for the first group of reactions decrease. This change of each energetic parameter has the opposite effect, as regards sign, on the rate of the process, but the positive influence of the change in activation energy greatly predominates, so that catalysis ensues. This is understandable because cyclic transition states are involved in the catalytic process, unlike the non-catalytic process, which favours a decrease of activation energy. The decrease of activation energy mentioned above can be explained by the high degree of order[114] in the structure of the transition state in catalytic reactions, which is also consistent with its cyclic structure.

In another group of reactions, the change from a non-catalytic to a catalytic process entails virtually no change in activation energy, because both processes proceed via cyclic transition states. On the other hand, the rate increases mainly as a result of the increase of activation entropy. The latter apparently shows that in this instance the structure of the transition state in the non-catalytic reaction is more ordered than that in the catalytic reaction.

The activation energies for all reactions catalysed by carboxylic acids are very high (Table 11), while the activation entropies are almost constant. On this basis one may assume that the mechanism of the catalysis by carboxylic acids is the same for all the acylating agents investigated, i.e. is described by the general scheme (6).

V. THE KINETIC ISOTOPE EFFECT OF DEUTERIUM

The cyclic structure of the transition state and the synchronous transfer of hydrogen atoms in the catalytic reaction with participation of bifunctional tautomeric catalysts is also confirmed by data obtained by isotopic labelling. Thus, when deuterated amines (in NH_2) and acetic acid (in OH) are used, a primary isotope effect is clearly observed in the case of acid halides (Table 12), becoming more intense on passing from the acid chloride to the fluoride, which forms stronger hydrogen bonds. This is consistent with the fact that, under the influence of a bifunctional tautomeric catalyst, two hydrogen atoms must be transferred in the rate-determining stage of the reaction. The increase in the ability of the reactant to form hydrogen bonds is in this case associated with the increase of the isotope effect (cf. C_6H_5COCl and C_6H_5COF). The comparatively small isotope effect is consistent with the possibility of hydrogen transfer via a cyclic transition state[116].

Table 12. The kinetic isotope effect of deuterium in the reactions of benzoyl chloride and acetic anhydride catalysed by acetic acid (CH_3COOH or CH_3COOD) (in toluene at 25°C).

Reaction	k_m^H/k_m^D
$C_6H_5COCl+p\text{-}Cl—C_6H_5NH_2$[96]	1.91±0.19
$C_6H_5COF+p\text{-}Cl—C_6H_4NH_2$[96]	3.34±0.50
$(CH_3CO)_2O+p\text{-}Cl—C_6H_4NH_2$[115]	1.00±0.10
$(CH_3CO)_2O+m\text{-}NO_2—C_6H_4—NH—CH_3$[115]	0.86±0.26

On the other hand, in reactions of acetic anhydride catalysed by a carboxylic acid the isotope effect is altogether absent, in contrast to the reactions of acid halides (Table 12). The latter can be accounted for by the fact that in reactions of acetic anhydride a symmetrical transition state (IIIb) may be postulated in the catalytic process, where B, A, and X are oxygen atoms. Swain's "solvation rule"[117] is therefore applicable in this instance; according to this rule, there is no isotope effect under the following conditions: firstly, if hydrogen is transferred between atoms of the same type; secondly, if the hydrogen in the transition state is not involved in reacting bonds[117], i.e. bonds which are ruptured and formed directly at the reaction centre.

In catalytic reactions involving anhydrides it is found that both parts of Swain's rule are satisfied. Furthermore, both hydrogen atoms in (IIIb) are transferred under completely identical conditions and synchronously, which leads to the cancelling of all the influences resulting from the replacement of hydrogen atoms by deuterium atoms.

In the analogous reactions of acid halides, where a transition state (IIIa) may be formed in conformity with the mechanism of the non-catalytic process, the first part of the rule never holds. The transfer of both protons should therefore not take place entirely symmetrically and, as already mentioned, a small but appreciable isotope effect is observed.

VI. CONCLUSION

As already mentioned at the beginning of the review bifunctional catalysts with a simple structure can be justifiably regarded as the simplest models of enzymes, because there is a definite similarity between these classes of substances. The similarity is manifested primarily by the fact that in both instances a major role is played by the preliminary association of the catalyst and the reactants, which results in the mutual approach and suitable relative orientation of the functional centres of the catalyst and the reactants, facilitating the reaction. Calculations[118] have shown that such mutual approach in enzymatic reactions reduces the length of the hydrogen bond to such an extent that a tunnel proton transfer at a rate exceeding that of diffusion-controlled processes becomes possible.

The next common feature of bifunctional catalysts and enzymes is the formation at the instant of the catalytic step of bond redistribution chains, which combine the reactant and catalyst molecules in the transition state into a single electronic system. The difference is that in enzymatic catalysis many-centre contacts are generated between the reactants and the catalysts, while in bifunctional catalysts only two-centre contacts, giving cyclic transition states, are produced. It is possible to distinguish two types of cyclic transition states.

1. States in which there is electron transfer via the ring formed when BRC undergo ring closure (bifunctional tautomeric catalysis). The occurrence of reactions via such states is particularly favourable, so that tautomeric catalysis is more effective than other types of bifunctional catalysis.
2. States in which BRC are either absent (solvation catalysis) or do not occur throughout the ring but only in the region where the catalyst is in contact with the reactants (bifunctional covalent catalysis).

Transition states of the first type are formed with participation of the catalyst, which contains two groups with opposite properties—electron-donating and electron-accepting—as a result of which these catalysts may be referred to as electrophilic-nucleophilic. Transition states of the second type may be formed, apart from the electrophilic-nucleophilic catalysts, by catalysts containing in their molecules active functional groups with identical properties. One can then speak, for example, of nucleophilic-nucleophilic [see, for example scheme (8)] or electrophilic-electrophilic catalysts. Although the possibility of the existence of catalysts of this kind is easy to imagine, they are nevertheless still unknown.

In order to explain certain aspects of enzymatic catalysis, a hypothesis has been used recently[119], according to which the hydrophobic sections of the enzyme form around the catalytic groups in its active centre a non-polar aprotic medium which ensures the most favourable conditions for the catalytic activity of these groups. The optimum conditions for bifunctional tautomeric catalysis occur, as shown above, precisely in non-polar aprotic media, which, firstly, confirms the above hypothesis, and, secondly, indicates yet another feature common to the two types of catalysis compared.

The problem associated with the selectivity of the action of organic catalysts is more complex. The fundamental difference between organic catalysts and enzymes is in fact associated with this factor and not solely with activity. Organic catalysts are naturally very selective but they are nevertheless greatly inferior in this respect to enzymes. A further search for ways of increasing the selectivity of the action of organic catalysts will apparently involve the synthesis of more complex molecules with a definite distribution of functional groups, some of which, for example, may play the role of substrate binding and orientation centres, while others are the catalytic groups proper.

In the search for more complex bifunctional and polyfunctional catalysts distinguished by a high activity and selectivity account must be taken of the conclusions reached in this review. (1) Bifunctional tautomeric catalysts exhibit the highest activity. (2) Their catalytic activity is manifested most strikingly in a solvent with a low solvating capacity. (3) Bifunctional catalytic activity is particularly high when conditions for the formation of strong hydrogen bonds are created in cyclic transition complexes. This depends on the nature of the catalyst itself and on the properties of the reactants and the medium. (4) Both the presence of the relevant functional groups in the bifunctional catalyst molecule and their steric disposition, ensuring the formation of a cyclic transition state, are very important for the manifestation of a high activity by such a catalyst. This is determined not only by the structure of the bifunctional catalyst but to an equal extent by the properties of the initial reactants.

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Electrochemical Determination of Surface Area of Metals

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The fundamental principles of the electrochemical determination of the surface area of metals are discussed. Conditions of determination and methods of calculation are analysed for smooth and powdered metals of the platinum group, nickel, the copper subgroup, and carbonaceous materials. A list of 108 references is included.

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I. INTRODUCTION

Study of the kinetics of heterogeneous processes requires a knowledge of the true surface area of the solid involved in the reaction. Several methods of determination based on the measurement of adsorption by volume or by weight have now been adequately developed and have been surveyed in detail in monographs and reviews[1-4].

Intensive work during the past decade has led to the widespread use of a new electrochemical method for determining the surface area of several metals in compact and powdered forms[5,6]. The possibility of determining true surface area from electrochemical measurements was first pointed out by Bowden and Rideal[7], and later by Shlygin and Frumkin[8]. Among the merits of this method, discussed quite fully by Brunauer[1], is its great sensitivity, which permits measurements on specimens of surface area down to 0.01 cm^2. The surface area of a catalyst can be measured electrochemically directly during the process when reaction takes place in an electrolyte solution[9,10]. These advantages, together with the rapidity of the measurements and the possibility of using readily available series-produced equipment, has attracted the attention of increasing numbers of research workers. However, no reviews hvve appeared on the electrochemical determination of surface area, which makes it difficult to choose the optimum procedure according to the nature of the metal and the conditions of measurement.

II. FUNDAMENTAL PRINCIPLES OF THE ELECTROCHEMICAL MEASUREMENT OF TRUE SURFACE AREA

The electrochemical method for determining the true surface area of a catalyst is based on measurement of the quantity of electricity consumed in changing the charge on the electrode in a given potential range. The theoretical basis of the method is Frumkin and Petrii's thermodynamic theory[11-13] of the surface state of electrodes that adsorb hydrogen and oxygen. It was shown[11-13] that in general the total (or thermodynamic) charge communicated to an electrode is consumed in charging the electrical double layer at the electrode-solution interface and in the adsorption of hydrogen, oxygen, or components of the electrolyte. The applicability of the thermodynamic theory to the surface state of a metal in an electrolyte solution was confirmed experimentally. In the case of a completely reversible system (e.g. a platinum electrode in the range of potentials for the adsorption of hydrogen) an unambiguous correspondence was established between the charge communicated to the electrode and its potential given by the charging curve. Either the charge consumed in adsorption (mostly of hydrogen) or the free charge (the differential capacitance of the electrical double layer) is determined experimentally. The surface coverage with adsorbed species or the capacitance of the double layer is found from investigations on electrodes of a given metal having a known true surface area (measured e.g. by the Brunauer-Emmett-Teller method). These values are then used as coefficients in determining the surface areas of other specimens of the same metal.

We shall now consider in greater detail the above two groups of methods, estimate their sensitivity, and assess the prospects of using them for various materials and experimental conditions.

1. Method of Charging Curves

Several modifications of the method of measuring charging curves can be used at the present time. They differ in the procedure for establishing conditions under which the whole of the electricity supplied to the electrode is consumed in changing its charge.

Frumkin and Shlygin[8,14,15] developed a technique of slow determination of charging curves on electrodes having a large true surface area. The curves were obtained from a solution saturated with an inert gas, to eliminate involvement in the electrochemical process of hydrogen or oxygen dissolved in the electrolyte. Powdered materials were placed in an electrically conducting gauze[16] to serve as current lead. Charge transfer can be effected by contact between the powder and an inert lead[17]. The quantity of electrochemically active impurities can be diminished[18] by decreasing the volume of the solution. Slow equilibrium charging curves can then be obtained at low current densities even on smooth electrodes.

A method was suggested[7,19] for obtaining rapid galvanostatic charging curves at high current densities. This would eliminate the effect of foreign solutes, which might have diffused to the electrode surface if the curves were determined slowly.

The above methods now find widespread use in electrochemical research.

Fig. 1 shows a typical charging curve for a platinum electrode in 1 N sulphuric acid, obtained at low current densities (the rapid galvanostatic curve is similar in shape)[20] (here and subsequently electrode potentials are given relative to the potential of a reversible hydrogen reference electrode in the same solution). The curve exhibits two arrests (region *I* and *III*) with a high pseudocapacitance. Ionisation of adsorbed hydrogen takes place in the region of the first arrest:

$$MH_{ads} \rightarrow H^+ + \bar{e} + M.$$

The second arrest corresponds to the discharge of water molecules with the formation of adsorbed oxygen or surface oxides:

$$M + H_2O \rightarrow MO_{ads} + 2H^+ + 2\bar{e}.$$

The two arrests are separated by a region *II* having a low capacitance, where a large proportion of the electricity is consumed in changing the charge on the double layer.

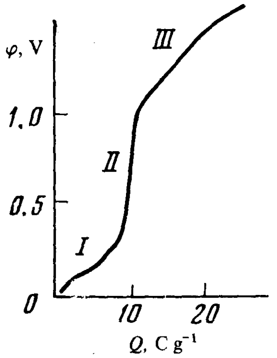

Figure 1. Charging curve for platinum in 1 *N* sulphuric acid at 20°C.[20]

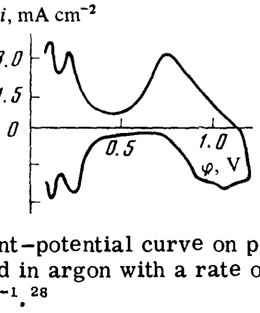

Figure 2. Current–potential curve on platinum in 1 *N* sulphuric acid in argon with a rate of application of potential of 1 V s^{-1}.[28]

Charging curves are now commonly obtained by a potentiodynamic method, first used for this purpose by Will and Knorr[21] and by Kolotyrkin and Chemodanov[22]. Electronic apparatus has been designed for this method[23-25] and investigations have been made on the surface state of various metals[16,24,26,27]. With linear scanning of the potential at a rate $v = \partial\varphi/\partial\tau$ the i–φ curves (Fig. 2)[28] determined by means of triangular voltage pulses represent essentially the differential form of the galvanostatic Q–φ curves: $I = v\partial Q/\partial\varphi$. Maxima on the potentiodynamic i–φ curve therefore correspond to maxima on the galvanostatic curve. The potentiodynamic method can be applied both to smooth[16,29,30] and to finely divided[16,31] electrodes. It yields highly reproducible results, largely because of the reproducible surface state of the electrodes obtained by periodic electrochemical oxidation and reduction[32,33] or by programmed pretreatment of the surface[24]. However, limitations on the rate of application of the potential, due to the disperse character of specimens, must be borne in mind when using this method.

The true surface area can be calculated from each of the above regions of the charging curve. However, the hydrogen region is generally used, because the deposition and removal of hydrogen are more reproducible than the corresponding processes with oxygen. In calculating the quantity of electricity corresponding to the hydrogen adsorbed, we must introduce a correction for the charging of the double layer and the evolution of molecular hydrogen. Finding the charge consumed in the evolution of hydrogen is a more difficult problem. In order to prevent the evolution of molecular hydrogen, therefore, the determination of slow charging curves does not extend beyond potentials 30–50 mV more positive than the reversible hydrogen potential.

The quantity of hydrogen adsorbed is determined from the area below the potentiodynamic i–φ curve bounding the hydrogen region (Fig. 2). This is equivalent to integrating the Q–φ curve:

$$Q = \frac{1}{v}\int_{\varphi_1}^{\varphi_2} i \cdot d\varphi$$

The end-point for measuring the quantity of electricity consumed in the adsorption of hydrogen on platinum was taken[34] to be the potential of the minimum preceding the evolution of hydrogen. This corresponds to the assumption that the quantity of electricity required for the adsorption of hydrogen at $\varphi < \varphi_{min}$ is balanced by the charge involved in the evolution of hydrogen at $\varphi > \varphi_{min}$. A similar postulate was made for other metals[35]. It has been suggested[36] that i–φ curves should be obtained at a low temperature (down to −72°C) to diminish the influence of hydrogen evolution on the quantity of hydrogen adsorbed.

The oxygen region of the charging or potentiodynamic curve can also be used to calculate the true surface area[30,37-42]. However, this gives rise to additional complications owing to the non-equilibrium character of the adsorption of oxygen and the time variation of the strength of its bonding to the surface[16,27,43,44]. As a result, the quantity of oxygen adsorbed depends on the current density used to obtain the charging curve or on the rate of application of the potential.

In order to calculate surface coverage of an electrode by hydrogen and oxygen it is necessary to know the quantity of electricity consumed in forming a hydrogen or oxygen monolayer. It is supposed that one hydrogen or oxygen atom is adsorbed on one metal atom. Polycrystalline electrodes are generally used in electrochemical investigations, so that most workers[16,37-40,45-47] start from the interatomic distance in determining the number of surface atoms. In the case of platinum this corresponds to 1.31×10^{15} atoms cm^{-2} true surface. Monolayers of hydrogen or oxygen on platinum then require consumptions respectively of 210 and 420 μC cm^{-2}. These values are used directly to calculate coverage by oxygen θ_H and θ_O. By no means in all cases is it possible to measure separately the quantities of electricity consumed in the adsorption of hydrogen and oxygen and in charging the double layer. If the regions in which these processes occur overlap (e.g. on nickel, silver, and carbonaceous materials), some numerical coefficient, determined by the charge necessary to change the electrode potential in the given range, must be used in calculating the true surface area.

In the electrochemical determination of surface area it must be borne in mind that the character of the charging curve is influenced significantly by the composition of the electrolyte[11]. This is due to the simultaneous adsorption of hydrogen and oxygen and of components of the electrolyte on the electrode surface. During recent years these phenomena have been investigated in detail on smooth and finely divided platinum[48-51] and palladium[52,53] electrodes. Thus for a palladium electrode in the presence of various anions and cations coverage with hydrogen decreases in the sequences

$$H_2SO_4 > H_3PO_4 > HCl > HBr \qquad KOH > NaOH > CsOH > Ba(OH)_2 > Ca(OH)_2.$$

In determining the surface area of a catalytic electrode, therefore, it is desirable to obtain galvanostatic or potentiodynamic charging curves in a standard electrolyte, whose components do not undergo strong specific adsorption. Organic impurities in the solution influence substantially the character of adsorption and the quantity of hydrogen adsorbed[54]. Special methods of purifying solutions have been described[33,52,55-57], ensuring that experiments can be conducted under sufficiently uncontaminated conditions. This is especially important in the investigation of smooth electrodes.

2. Measurement of Differential Capacitance

Another method for determining true surface area involves measuring the differential capacitance of the double layer. The relaxation time of the double layer is considerably shorter than typical times of adsorption and exchange accompanied by complete or partial transfer of charge across the interface. We can measure the capacitance of the double layer by high-frequency a.c.[58,59] or pulse[59] methods with short resolving times ($\sim 10^{-6}$ s), and use the result to estimate true surface area. It is usually assumed in this method[60-65] that the capacitance of the double layer is the same on different metals, equal to the capacitance of the mercury electrode (16–20 μF cm^{-2}). However, recent accurate measurements indicate[66] that different metal electrodes may differ in capacitance by 50–100%. Relaxation methods for measuring the differential capacitance of the double layer are applicable only to smooth electrodes, which is an important restriction on their use for determining true surface area.

Isolated attempts were made[8] to determine the capacitance of the double layer by means of slow charging curves. However, these methods cannot be regarded as successful, since in most cases processes involving adsorption of electrochemically active species also occur in the "double layer" region. It was shown[67] by Frumkin's thermodynamic method[11] that oxygen already begins to be adsorbed on platinum at potentials more positive than 0.3 V.

Comparison of the two groups of electrochemical methods for determining true surface area—by obtaining charging curves and by measuring differential capacitance—indicates that the former are simpler, more generally applicable, and reliable. It therefore forms the basis of most electrochemical techniques for measuring true surface area. Recently the possibility has been discussed of determining this property from the rate of an electrode reaction with a known specific exchange current[68].

III. DETERMINATION OF TRUE SURFACE AREA OF VARIOUS MATERIALS

Specific methods for measuring true surface area of various metals are governed by the nature of the latter, the ability to adsorb hydrogen and oxygen. Specific surfaces of most metals that have been investigated electrochemically are determined from the adsorption of hydrogen. They include metals of the platinum group—platinum, palladium, rhodium, iridium, ruthenium, and osmium—together with nickel. With platinum and rhodium the potential range for the adsorption and desorption of hydrogen is quite clearly defined. With ruthenium and nickel the potential ranges for the adsorption of hydrogen and oxygen overlap. The adsorption of hydrogen on palladium (and to some extent also on nickel) is complicated by the dissolution of hydrogen in the bulk of the electrode. Hydrogen is hardly adsorbed at all on gold, copper, and silver, on which surface area is determined from the adsorption of oxygen or the polarisation capacitance in a certain potential range. The last method is used also to determine surface areas of carbonaceous materials.

1. Platinum Metals and Nickel

Platinum and rhodium

Galvanostatic charging curves have been used to investigate the surface coverage of finely divided platinum and rhodium powders by adsorbed hydrogen and oxygen[10,16]. The potentials at which adsorbed hydrogen is completely removed from the surfaces of these metals are respectively 0.40 and 0.27 V (in 1 *N* sulphuric acid). The quantity of hydrogen adsorbed was determined by the method of tangents. No correction was made for the capacitance of the double layer, so that values of θ_H were rather too high.

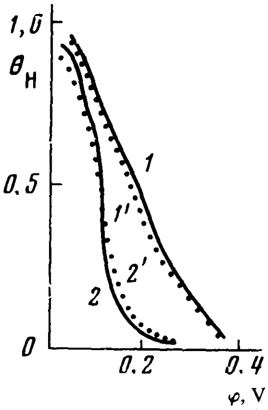

Figure 3. Potential dependence of surface coverage with hydrogen of: 1) platinum powder ($s = 20$ m^2 g^{-1}); 1′) smooth platinum electrode; 2) rhodium powder (20 m^2 g^{-1}); 2′) smooth rhodium electrode[16].

However, the contribution of this capacitance does not[51] exceed 5–7%, which is smaller than the error in the BET method. Knowing the true surface area of powders measured by the BET method, we can calculate values of θ_H on platinum and rhodium at various potentials.

Monolayers of hydrogen on platinum and rhodium surfaces correspond in electrical units to 210 and 220 μC cm^{-2} respectively. Fig. 3 shows that surface coverage of both platinum and rhodium powders with hydrogen reaches a monolayer ($\theta_H \approx 1$) near the reversible hydrogen potential. Similar results have been obtained on a single crystal of platinum[70]. The surface area of platinum and rhodium is independent of the method of obtaining the powders or their degree of dispersion, so that the hydrogen region of the charging curve can be used to determine the true surface area of these powdered metals[16]. Galvanostatic charging curves on the powders were compared with $i-\varphi$ curves obtained by means of triangular voltage pulses on smooth electrodes. Good agreement was obtained for $\theta_H-\varphi$ curves on smooth and dispersed electrodes (Fig. 3). The technique can be used also to determine the true surface area of platinum–rhodium alloys[71].

The possibility has been considered[37-41] of measuring the true surface area of platinum from the adsorption of oxygen. Surface coverage was then determined as the ratio of the quantity of electricity consumed in the adsorption of oxygen to double the quantity corresponding to a monolayer of hydrogen: $\theta_O = Q_O/2Q_H$. However, diverse values have been published—1.76,[37] 1.83,[38] 1.05,[41] and 1.24 [40] V—for the potential at which $\theta_O \approx 1$. Such divergence is due to the non-equilibrium character of the adsorption of oxygen and to accumulation of the gas on the electrode surface with time.

Ruthenium

Comparison of the electrochemical determination of the true surface area of ruthenium black[72] with the BET method showed that the quantities of electricity consumed in adsorption of hydrogen near the reversible hydrogen potential are 280 and 218 μC cm^{-2} in aqueous sulphuric and hydrochloric acids respectively. The former value corresponds to a monolayer. Determination of true surface area from the charge consumed in the double-layer region gave markedly overestimated values, owing to the presence of adsorbed oxygen on the ruthenium surface in this range.

Palladium

The possibility of determining the true surface area of palladium powders from the adsorption of hydrogen has been subjected to detailed investigation[16,52,53,73]. The complexity of such determination is due to the dissolution of hydrogen in the bulk of the metal. A typical charging curve obtained on powdered palladium in 1 *N* sulphuric acid is reproduced in Fig. 4. Over the range of potentials 0–0.08 V hydrogen dissolves with the formation of α and β phases. It is adsorbed at $0.08\ \text{V} < \varphi < 0.28$ V; some adsorption of hydrogen is observed also at $\varphi < 0.08$ V.[52] A technique was proposed[52,53] for separating the quantity of hydrogen adsorbed and desorbed in the potential range of chemisorption, and determining the surface coverage with chemisorbed hydrogen at each potential on the assumption that θ_H is independent of the degree of dispersion of the specimens. This assumption was confirmed for palladium powders of true surface area 0.3–100 m^2 g^{-1}. Fig. 5 illustrates the dependence of surface coverage of palladium with hydrogen over the potential range 0–0.28 V in 1 *N* sulphuric acid (curve *1*). It follows from these results that the quantity of hydrogen chemisorbed at 0.075 V corresponds to $\theta_H = 0.82$, but at potentials close to zero $\theta \approx 1$. The calculations were based on the hypothesis that the quantity of electricity consumed in coverage with a monolayer of hydrogen was 210 μC cm^{-2}.

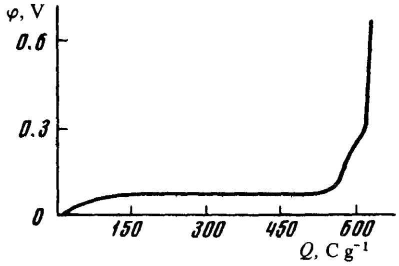

Figure 4. Charging curve on palladium powder (30 m^2 g^{-1}) over the range 0–0.7 V in [1 N] sulphuric acid at 25°C.[73]

Investigation of the influence of anions (PO_4^{3-}, Cl^-, Br^-, and SO_4^{2-}) [52] and of cations (K^+, Na^+, Cs^+, Ca^{2+}, and Ba^{2+})[53] on the adsorption of hydrogen on palladium showed that the course of the charging curves in the region of the $\alpha-\beta$ phase transition is almost independent of solution composition, whereas the chemisorption of hydrogen is affected significantly by the nature of anion and cation. The surface coverage θ_H diminishes with increase in the adsorbability of the anions (Fig. 5). A similar pattern is observed with cations[53].

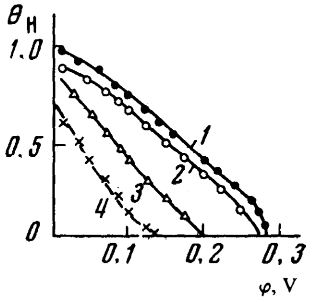

Figure 5. Potential dependence of surface coverage of palladium powder with hydrogen in 1 *N* acids: 1) sulphuric; 2) orthophosphoric; 3) hydrochloric; 4) hydrobromic.[52]

Thus the true surface area of palladium powders can be determined from the adsorption of hydrogen. The divergence between the results and values obtained by the BET method does not exceed 10%.[16]

The $\theta-\varphi$ curves calculated for smooth palladium electrodes from potentiodynamic $i-\varphi$ curves obtained with the potential applied at 20 mV s^{-1} were found[16] to coincide with $\theta-\varphi$ curves for finely divided powders. This indicates the possibility of using potentiodynamic curves to determine true surface areas of smooth palladium electrodes.

The total quantity of electricity representing the adsorption of hydrogen dissolved in and adsorbed on palladium in the range 0–0.3 V cannot be used to measure the surface area of palladium, as had been suggested[74], since the quantity of hydrogen dissolved is independent of the surface area. Thus this quantity is approximately the same for powders having surface areas of 39 and 3 m^2, whereas the quantity of hydrogen adsorbed differs more than tenfold[16].

The true surface area of smooth palladium has been determined[42] from the adsorption of oxygen under conditions such that in 1 N sulphuric acid a monolayer is formed at $\varphi \simeq 1.0$ V, in agreement with results obtained by other workers[52,53,73].

Nickel

The electrochemical behaviour of nickel near the potential of the reversible hydrogen electrode has been less well studied than that of the platinum metals. There is no generally accepted view on the mechanism of the adsorption and dissolution of hydrogen and the formation of oxide layers in this potential region[75–85]. The widespread use of nickel in electrocatalysis (liquid-phase hydrogenation, chemical current sources, etc.) has given rise to repeated attempts to develop electrochemical methods for determining its true surface area. These methods usually involved determining the capacitance of the double layer (using alternating current[86–88], from the fall in potential after polarisation had been switched off[89], and from charging curves[90]). The calculation was based on various values for the differential capacitance of the double layer (from 10[91] to 100 μF cm^{-2}).[90] Therefore these procedures can hardly be recommended for determining the true surface area of nickel without adequate experimental support. A method based[92] on measurement of the adsorption of thallium and sodium ions is merely comparative.

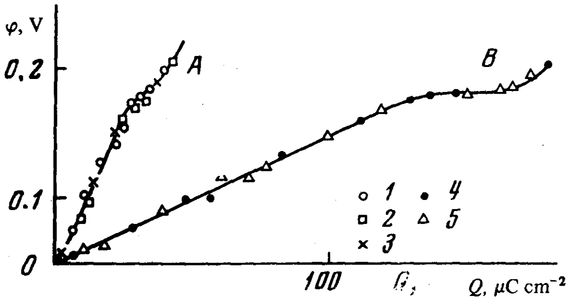

Figure 6. Charging curve per unit surface area (measured by the BET method) of nickel: A) Raney; B) carbonyl; 1) sintered electrode of A; 2) sintered electrode of a mixture of 50% A + 50% B; 3) powder in a grid of A; 4) powder in a grid of B; 5) sintered electrode of B.[81]

The most soundly based method for determining the true surface area of smooth and finely divided nickel was developed by workers who showed[81–85] that hydrogen does not undergo bulk dissolution in nickel at $\varphi \geqslant 0.03$ V. A similar conclusion was reached by another worker[79]. Surface areas (measured by the chemisorption of oxygen from the gas phase) of various nickel powders were compared[81–83] with the slopes of the linear portion of the equilibrium galvanostatic charging curve (Fig. 6) over the range 0.03–0.17 V. The pseudocapacitance calculated per unit true surface area was 1120 μF cm^{-2}. Such a value was explained by the occurrence of electrochemical processes involving adsorbed layers of neutral species.

$$H_{ads} + OH^- \rightarrow H_2O + \bar{e},$$

$$Ni + x\,OH^- \rightarrow Ni\,(OH)_x + x\,\bar{e}.$$

Determination by a vacuum–electrochemical method of the surface coverage of nickel with hydrogen and with oxygen showed that $\theta_H > 0.95$ and that $\theta_{OH} < 0.5$ and 0.2 at $\varphi \simeq 0$ and 0.17 V respectively. These results make it possible to determine the true surface area of finely divided nickel in this potential range.

If it is assumed that the nature of the adsorbed species is the same on smooth and powdered specimens, the results can be used to investigate smooth electrodes[83,85]. Potentiodynamic i–φ curves are then obtained in alkaline solution over the range 0.03–0.18 V, and the quantities of electricity at different rates V of application of the potential are extrapolated to $V = 0$. The result is compared with the value 1120 μF cm^{-2}. The electrode must be subjected to a special (stepwise) treatment at 0.2, 0.1, and 0 V in order to obtain reproducible results[83]: otherwise a different value may be obtained for the pseudocapacitance per unit surface area of the nickel powder[80].

The electrochemical method for determining the true surface areas of platinum metals and nickel has found practical application in investigating electrocatalytic processes on porous gas-diffusion and liquid electrodes. It has been used to determine the surface area of the catalyst in porous electrodes[93] during preparation and operation[41,94,95], in measuring the distribution of liquid and gas porosity[94], for determining the surface area of platinum metals on a carrier[96], and also in calculating the kinetic parameters of electrochemical reactions[93].

2. Metals of the Copper Subgroup

Hydrogen is not readily adsorbed on copper, silver, and gold, in contrast to metals of the platinum group, so that surface coverage with hydrogen cannot be used to determine the true surface areas. Therefore either the potential range corresponding to the adsorption of oxygen is used (copper and gold), or else some segment of the charging or potentiodynamic i–φ curves on which the polarisation capacitance has been determined in preliminary experiments (silver).

Gold

An electrochemical method has been developed[16,29] for determining the true surface area of finely divided and smooth gold from the adsorption of oxygen. The surface coverage in acid solutions was calculated from charging curves or from potentiodynamic curves over the range 1.3–1.7 V. On the assumption that one oxygen atom is adsorbed on one metal atom the coverage of finely divided gold reaches a monolayer at 1.7 V. The adsorption of oxygen obeys similar laws on smooth and finely divided gold: the specific adsorption is the same on such electrodes. Good agreement is found between surface areas obtained from charging curves and by the BET method.

Copper

The quantity of surface oxide Cu_2O forming a monolayer in a given potential range is determined[97]. Conditions required[97] indicate that surface area is most conveniently measured in alkaline solutions. The quantity of electricity corresponding to a monolayer of copper(I) oxide is 180 μC cm^{-2}.[98] The quantity of oxide is calculated from the arrest on the charging curve in the range 0.87–0.47 V. It can be found also by obtaining potentiodynamic curves with the potential applied at 2–10 mV s^{-1}. This method has been used to determine the true surface area of copper coatings having a roughness factor of 2–10. It has found application in studies of the corrosion of copper[99].

Silver

Determination of true surface area from the adsorption of oxygen on silver, in contrast to gold and copper, is difficult because of the formation of multilayer deposits. The adsorption of oxygen on silver powders in the range 0.25–0.8 V gives in several cases[100] good agreement with BET results. The roughness factor of smooth silver electrodes has been estimated[101,102] from the quantity of electricity determined from i–φ curves obtained by the application of triangular voltage pulses over the potential range 0–0.2 V, in which it was assumed[101,102] that the quantity of electricity was consumed only in charging the double layer of the silver electrode.

A more rapid method proposed[31] for determining the surface area of silver powders involves applying the triangular pulse to the electrode after cathodic reduction of the latter at negative potentials, with i–φ curves obtained in the range 0.2–0 V applied at the rate 3–40 mV s^{-1}. As before[101,102] this potential range is regarded[31] as corresponding to charging of the double layer. It was assumed for the calculation that the true capacitance of silver in this potential range is 50 μF cm^{-2}. The results agree well with those obtained by the BET method.

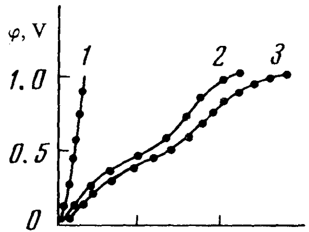

Figure 7. Charging curves on silver powders differing in specific surface (m^2 g^{-1}): 1) 2.5; 2) 3.0; 3) 10.[100]

The true surface areas of silver powders prepared in various ways were measured[100] by the BET method and compared with electrochemical measurements by means of slow charging curves in 0.1 N aqueous potassium hydroxide. Charging curves on silver powders are plotted for various specific surfaces in Fig. 7. Comparison of BET surface areas with the quantity of electricity consumed in the range 0–0.25 V showed that for almost all the silver powders $Q/s_{\mathrm{BET}} = 0.02 \pm 0.003$ mC cm^{-2}. Hence the true surface area of silver can be determined from the polarisation capacitance in the potential range 0–0.25 V.

3. Carbonaceous Materials

Measurement of the specific surface of carbonaceous materials is one of the most important and difficult tasks. Development of an electrochemical method is impeded by the existence of such materials in various modifications (coal, carbon black, graphite, pyrographite, vitreous carbon), whose electrochemical properties depend in considerable degree on their structure and the method of measurement. Appreciable difficulties may result also from the presence of micropores, of dimensions comparable with the radii of hydrated ions, in several carbonaceous materials (e.g. in activated carbon). This would lead to a change in the capacitance of the double layer.

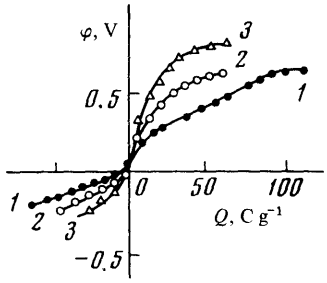

Figure 8. Charging curves obtained in 0.01 N sulphuric acid on: 1) activated carbon (surface area 710 m^2 g^{-1}); 2) carbon black (760); 3) graphite (670).[107]

The adsorption of oxygen and hydrogen on various carbonaceous materials has been investigated in electrolyte solutions[103-108]. Fig. 8 shows typical charging curves on activated sugar charcoal, PM-100 carbon black, and graphite in 0.01 N sulphuric acid[107]. The capacitance is minimal in the potential range 0.05–0.25 V. This segment of the charging curve corresponds to the capacitance of the double layer. Values of the capacitance for coal, carbon black, and graphite are 7.0, 4.5, and 2.5 μF cm^{-2} true surface area. Hydrogen is adsorbed at potentials more negative than those corresponding to the double-layer region, and oxygen at more positive potentials. Results obtained for coal and carbon blacks having different surfaces in 0.1 N sulphuric acid indicate that the "oxygen" portion of the charging curve can be used to determine the true surface areas of these adsorbents. With coal the mean polarisation capacitance is 28 ± 2 μF cm^{-2} for surface areas of 450 and 710 m^2 g^{-1}, which corresponds to an accuracy of 10%; but with carbon black the mean value is 13 ± 2 μF cm^{-2} over the range 160–760 m^2 g^{-1}, corresponding to an accuracy of 15%. For KhS-72 carbon black and AG-3 carbon the polarisation capacitance in the same potential range was respectively 15 and 19 μF cm^{-2}.[108] Deviations from the results of

Ref. 107 may be due to technical differences in the production of the carbonaceous materials.

An attempt was made[106] to use a.c. polarisation to measure the surface area of porous carbonaceous materials (coal and graphite of various brands), which reduces to determining the capacitance of the double layer. As noted above, however, the specific capacitance of the double layer depends on the nature of the carbonaceous material[107]. Hence the capacitance values used to calculate specific surface area from electrochemical data require special experimental justification.

oOo

The electrochemical method for determining true surface area is now sufficiently developed for platinum metals, the copper subgroup, nickel, and certain types of carbonaceous materials. It has been successfully used to study several electrolytic processes at electrodes of these materials. The number of research topics to which the electrochemical determination of surface area is applicable will increase as investigation of the structure of the double layer and of adsorption from electrolyte solutions on other metals and alloys is extended. Another important line of development of the electrochemical method is to measure the surface area of metallic or semiconducting catalysts on carriers, of platinum on carbon, oxides on carbon, and nickel and silver powders stabilised by oxides.

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The Reactivity of Carbanions

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Ionic species involved in the reactions of alkali and alkaline-earth metal salts of CH-acids with various electrophiles are discussed, as well as the factors influencing the relative concentrations of these species. The reactivities of carbanions and their ion-pairs in nucleophilic substitution and addition and in electron and proton transfers are examined in terms of quantitative experimental results. A list of 140 references is included.

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I. INTRODUCTION

Many reactions of organic compounds involve carbanions, negatively charged species in which the charge—more often part of the charge—is concentrated on the carbon atom. It is now well known that the mechanism, the stereochemical direction, and the kinetics of these reactions are determined by the reactivities of the diverse forms in which carbanionic species exist in solution, as well as by their relative concentrations. However, although considerable progress has been made in studying the physical properties of ionic species, the state of information on their reactivity is still unsatisfactory.

The main purpose of the present Review is to analyse kinetic data obtained for the reactions of CH-acid salts of alkali and alkaline-earth metals, since they are almost the only sources of carbanions that have been studied in this respect. These salts have ionic structures (organolithium compounds form an exception, for the carbon-lithium bond in them is not always ionic in character[2]): i.e. they are ionophores[1], the ionic species of which exist in steady concentrations in solution, which considerably facilitates kinetic analysis.

We shall disregard the reactions of ambident anions, which develop a dual reactivity, for they have been discussed quite thoroughly[3-6]. The section on proton-transfer reactions leaves out of consideration investigations on kinetic acidity in isotope-exchange reactions in CH-acids, processes which have been discussed in sufficient detail[7-10]. Furthermore, the reactivities of carbanions are assessed from their rates of formation, which is not altogether correct, owing to the occurrence of a recovery stage that cannot be strictly allowed for, quite apart from the possible participation of both free ions and ion-pairs in these reactions, whose contributions have not been separated.

The fundamental studies by Cram showed that the character of the carbanionic species involved in isotope exchange has a decisive influence on the stereochemical result of the reaction. However, the absence of accurate kinetic parameters for each ionic species compels us to exclude the stereochemistry of the reactions of carbanions from consideration.

II. TYPES OF REACTIVE SPECIES

The complicated character of the problem of determining the reactivity of carbanions lies in the existence of their source compounds in solution not only as free ions C^- and M^+ but also as contact or solvent-separated ion-pairs C^-M^+ or $C^-\|M^+$, aggregates of ion-pairs $(C^-M^+)_n$ or $(C^-\|M^+)_n$, and more complex ionic structures, e.g. $(C^-)_{n-1}(M^+)_n$ and $(C^-)_n(M^+)_{n-1}$. In general these species differ in reactivity, which suggests that the environment has a great influence on the rates of reactions involving a carbanion. All the ionic species are interrelated by the rapidly established equilibria

$$\begin{tikzcd} C^-M^+ \arrow[rr, shift left, "K_1"] \arrow[dr, shift left] & & C^-\|M^+ \arrow[ll, shift left] \arrow[dl, shift left] \\ & C^- + M^+ \arrow[ul, shift left, "K_2"] \arrow[ur, shift left, "K_3"'] & \end{tikzcd} \qquad (1)$$

$$\begin{tikzcd} n\,(C^-M^+) \arrow[r, shift left] & (C^-M^+)_n \arrow[l, shift left] \arrow[r, shift left] \arrow[dr, shift left] & C^- + (C^-)_{n-1}\,(M^+)_n \arrow[l, shift left] \\ & & M^+ + (C^-)_n\,(M^+)_{n-1} \arrow[ul, shift left] \end{tikzcd} \qquad (2)$$

$$\begin{tikzcd} n\,(C^-\|M^+) \arrow[r, shift left] & (C^-\|M^+)_n \arrow[l, shift left] \arrow[r, shift left] \arrow[dr, shift left] & C^- + (C^-)_{n-1}\|(M^+)_n \arrow[l, shift left] \\ & & M^+ + (C^-)_n\|(M^+)_{n-1} \arrow[ul, shift left] \end{tikzcd} \qquad (3)$$

which are easily displaced in a particular direction by varying the reactant concentrations, changing the nature of the medium or its temperature, introducing unreactive ions or solvating additives, applying an external electric field, etc. These equilibria must be considered because the contributions of the above ionic species to the observed rate constant can be determined, and the factors influencing the reactivity of the carbanion revealed, only if the species actually present in solution and their concentrations are known.

1. Ion-pairs and Free Ions

The equilibrium between contact and solvent-separated ion-pairs was first investigated by Smid et al.,[11-24] who chose as model the fluorene salts of alkali and alkaline-earth metals, using mainly a simple spectral and conductometric technique. Subsequent investigations of this equilibrium in solutions of other salts of carbanions[12,25-32] and salts of radical-anions[33,34] established almost the same laws, governing the influence of the medium, the nature of the ions, and the temperature, as those discovered by Smid et al. We shall not discuss details, since numerous excellent reviews and monographs have appeared on this topic[22,33-85], but will report briefly the principal laws.

The constant K_1 depends on the structure of the carbanion, the size and charge of the cation, the nature of the solvent, and the temperature. The influence of the structure of the carbanion on the equilibrium between contact and solvent-separated ion-pairs is determined by both electronic and steric factors. In general increase in the degree of charge delocalisation in the anion should favour the formation of solvent-separated ion-pairs. Thus in oxolan the value of K_1 for the sodium salts of 1,2- and 3,4-benzofluorenes exceeds several times that for fluorenylsodium[11]. The reason for the higher proportion of contact ion-pairs of the sodium salt of 1,3-diphenylbut-1-ene than of the sodium salt of 1,3-diphenylprop-1-ene in the same solvent is the increased effective charge on the carbanion due to the inductive effect of the methyl group[28].

The negative charge of a mesomeric anion containing a heteroatom may be concentrated mainly on this atom, with a consequent strengthening of electrostatic interaction between the oppositely charged parts of the ion-pair, which complicates their separation by the solvent. This provides an explanation of the presence solely of contact ion-pairs in solutions of alkali-metal salts of 9-cyanofluorene[36] and methyl fluorene-9-carboxylate[37] in dimethoxyethane.

Among structural factors that may influence the position of the equilibrium between the different types of ion-pairs we must include the presence at the anionic centre of substituents capable of impeding direct contact between the ions. Thus under the same conditions the proportion of solvent-separated ion-pairs is always smaller in solutions of alkali-metal salts of fluorene than in those of the corresponding salts of 9-2′-methylpentylfluorene[12].

Solvent-separated ion-pairs can be formed only in solvents that are capable of surrounding at least one of the ions with a dense solvate sheath. In the usual media (dipolar aprotic solvents, solvents of ether type) it is the metal cation in the usual ion-pairs of carbanions that interacts with the solvent. Therefore the position of the equilibrium between intimate and loose ion-pairs depends primarily on how well specifically solvated is the gegenion. In solvents of ether type (oxolan, dimethoxyethane, diethyl ether, oxan) the proportion of solvent-separated ion-pairs always increases with decrease in the radius of the alkali-metal cation in the sequence

$$Cs^+ < Rb^+ < K^+ < Na^+ < Li^+.$$

This is the situation in solutions of alkali-metal salts of fluorene[11], triphenylmethane[30], 1,3-diphenylbut-1-ene[26,28] and 1,3-diphenylprop-1-ene[27,28], indene[30], 4,5-methylenephenanthrene[32], and 1- and 2-methylnaphthalenes[31].

On passing from salts of alkali metals to those of alkaline-earth metals (difluorenyl-barium, -strontium) the proportion of solvent-separated ion-pairs diminishes considerably[13,14], as a consequence both of increase in the electrostatic interaction in salts of doubly charged cations and of the great hindrance to their solvation. Here, too, the equilibrium shifts towards solvent-separated ion-pairs with decrease in the radius of the cation[14]. Formation of solvent-separated ion-pairs is considerably favoured by increasing the polarity of the solvent and its solvating power for the cation, the latter factor often being dominant. The proportion of loose ion-pairs in alkali-metal salts of fluorene increases (i) as the solvent becomes more basic[15,16] in the sequences

dioxolan < oxan < 2,5-dihydrofuran < oxolan < oxetan,
dioxan < 3,4-dihydropyran < oxetan,
oxolan ≪ hexamethylphosphoramide, dimethyl sulphoxide

(ii) on passing from uni- to bi- and multi-dentate solvents[15,16] in the sequences

oxolan ≪ 2-methoxymethyloxolan,
m-dimethoxybenzene < oxolan < *o*-dimethoxybenzene

and (iii) with increase in the number *n* of oxyethylene units in glymes (dimethyl ethers of polyethylene glycols) $CH_3O[CH_2CH_2O]_nCH_3$ added in small quantities to ethereal solvents[17,18]

$$1 < 3 < 4 < 5 < 6 < 7 < 9 < 22.$$

Analogous regularities are observed on examining equilibria between ion-pairs of alkali-metal salts of 9-2′-methylpentylfluorene[12], triphenylmethane[30,38], 1,3-diphenylalkenes[25-28], and other systems[30-32].

However, the greatest effect on the equilibrium between ion-pairs is exerted by crown polyethers[39] and cryptates[40]: small additions to solutions of carbanion salts of alkali metals[19,20] or alkaline-earth metals[10] increase K_1 by several powers of ten.

Lowering the temperature causes the equilibrium between ion-pairs in solutions of carbanion salts to shift towards solvent-separated pairs in all the systems studied, since at low temperatures solvation is less disturbed by the thermal motion of the molecules. Incorporation of solvent into the ion-pair is accompanied by decreases in enthalpy and entropy. Table 1 gives some idea of the thermodynamic parameters of the transition of intimate into loose ion-pairs, as well as the magnitude of the equilibrium constants.

Table 1. Thermodynamic parameters of the equilibrium (1) between contact and solvent-separated ion-pairs at 25° C.

Anion	Solvent	Cation	K_1	$-\Delta H_1$, kcal mole^{-1}	$-\Delta S_1$, e.u.	Ref.
Fluorenyl	oxolan	Li^+	4.6	7.5	22	16
Fluorenyl	oxan	Li^+	0.45	6.6	28	16
Fluorenyl	oxepan	Li^+	0.24	4.3	16	16
9-2′-Methylpentylfluorenyl	2,5-dimethyl-oxolan	Li^+	50	10.0	50	12
2-Methyl-1-3-diphenylallyl	oxepan	Li^+	—	8.4	30.5	25
2-Methyl-1-3-diphenylallyl	oxolan	Li^+	—	6.7	24.5	25
2-Methyl-1-3-diphenylallyl	oxolan	Na^+	—	10.7	41	25
1,2,3-Triphenylallyl	oxepan	Li^+	—	6.0	20	25
1,2,3-Triphenylallyl	oxolan	Ba^{2+}	—	4.1	21	25
1,3-Diphenylallyl	oxolan	Na^+	—	6.1	22	27
1,3-Diphenylallyl	oxolan	K^+	—	4.1	16.5	27
Triphenylmethyl	oxolan	Na^+	0.38	8.2	28	38
Triphenylmethyl	dimethoxy-ethane	K^+	0.1	6.7	16	38

The dissociation equilibria—between ion-pairs and free ions (equilibrium constants K_2 and K_3)—are influenced by the same factors—structure of carbanion, size and charge of gegenion, nature and temperature of medium—as is the equilibrium between ion-pairs. These factors have considerably less influence on the dissociation of solvent-separated ion-pairs, in which interionic interaction is appreciably weaker. It must also be borne in mind that the work of diluting oppositely charged ions to an infinite distance (i.e. dissociation) is done mainly at the stage of introducing the first solvent molecule between them. It is by no means always possible to isolate the parameters relating to dissociation of ion-pairs of a certain type, since the measured dissociation constant [calculated from the Fuoss conductance equation] is a composite quantity: $K_D^{-1} = K_2^{-1} + K_3^{-1}$. Hence the enthalpy and entropy of dissociation are also composite[16]:

$$\Delta H_D = \Delta H_3 + \Delta H_1(1+K_1)^{-1}; \quad \Delta S_D = \Delta S_3 + \Delta S_1 \cdot (1+K_1)^{-1}.$$

It is not surprising, therefore, that not only K_D but also the observed values of ΔH_D and ΔS_D vary with temperature, owing to the shift in the equilibrium between the ion-pairs.

The data in Table 2 show that in the large majority of cases the enthalpy and the entropy of dissociation are negative; moreover, they usually decrease in absolute magnitude with fall in temperature. This was to be expected, since at low temperatures the terms $\Delta H_1(1+K_1)^{-1}$ and $\Delta S_1(1+K_1)^{-1}$ make smaller contributions to the observed functions. The magnitudes of ΔH_D and ΔS_D depend both on K_1 and on the thermodynamic parameters of the transition of contact into solvent-separated ion-pairs (Table 1). If ΔH_D (and of course ΔS_D also) reach limiting values unaffected by further fall in temperature[14,21], this would suggest that ion-pairs of only one type (solvent-separated) exist in solution under these conditions. If variation of the temperature does not affect the enthalpy of dissociation, this also indicates that free ions are formed from ion-pairs of a single type, but they may be either contact[14,21,36] or solvent-separated[14,16,21]. The type can be decided from the magnitudes of ΔH_D, which are higher for close ion-pairs (by factors of 2–3[14,16,21,28,41]), and also from spectral data[22].

Table 2. Parameters of the dissociation of certain salts of alkali and alkaline-earth metals with CH-acids.

Anion	Cation	Solvent*	t, °C	$10^8 K_D$, M	$-\Delta H_D$, kcal mole^{-1}	$-\Delta S_D$, e.u.	Ref.
9-Methylfluorenyl	Li^+	DME	25	380	—	—	37
9-Phenylfluorenyl	Li^+	DME	25	560	—	—	37
Fluorenyl	Li^+	DME	15	620	2.9	33	21
Fluorenyl	Li^+	DME	−65	2140	~0	—	21
Fluorenyl	Cs^+	DME	15	25	4.6	45	21
Fluorenyl	Cs^+	DME	−65	300	~1.0	—	21
Fluorenyl	Li^+	oxolan	25	300	3.5	37	21
Fluorenyl	Li^+	oxolan	−70	1550	~0	—	21
Fluorenyl	Cs^+	oxolan	25	1.4	2.9	46	21
Fluorenyl	Cs^+	oxolan	−70	5.5	1.0	38	21
Fluorenyl	Ba^{2+}	oxolan	20	5.3	10	54.4	14
Fluorenyl	Ba^{2+}	oxolan	−70	22	10	54.4	14
Fluorenyl	Sr^{2+}	oxolan	20	17.3	13.3	76	14
Fluorenyl	Sr^{2+}	oxolan	−70	256	0	25	14
Triphenylmethyl	Na^+	ether	25	$1.5\cdot10^{-4}$	—	—	41
Triphenylmethyl	Na^+	oxolan	25	760	6.2	44	38
Triphenylmethyl	Na^+	oxolan	−60	5040	0.6	23	38
Triphenylmethyl	K^+	oxolan	25	340	—	—	38
Polystyryl	Na^+	HMPA	40	10^6	—	—	42
Polystyryl	Na^+	oxolan	25	15	8.2	—	43
Polystyryl	Cs^+	oxolan	25	0.47	1.8	—	43
Tri-*p*-nitrophenylmethyl	Li^+	oxolan	25	21	—	—	44
Tri-*p*-nitrophenylmethyl	Cs^+	oxolan	25	570	—	—	44
9-Cyanofluorenyl	Li^+	DME	25	30	6.5	—	36
9-Cyanofluorenyl	Na^+	DME	25	100	3.7	—	36
9-Cyanofluorenyl	Na^+	ethanol	25	$>10^6$	—	—	45
9-Cyanofluorenyl	Cs^+	DME	25	500	4.9	—	36
Poly-2,3-dimethylbutadienyl	Li^+	oxolan	25	$\sim10^{-4}$	—	—	46
Polyisoprenyl	Li^+	oxolan	25	0.08	—	—	46
Polybutadienyl	Li^+	oxolan	25	3	—	—	46
Poly-α-methylstyryl	Li^+	oxolan	25	8.3	—	—	46
Polystyryl	Li^+	oxolan	25	35	—	—	46
Cyclopentadienyl	Li^+	oxolan	25	47	—	—	46
Indenyl	Li^+	oxolan	25	990	—	—	46

*DME = dimethoxyethane; HMPA = hexamethylphosphoramide.

The thermodynamic approach to the problem of the dissociation of ion-pairs[47,48], in which the solvent is regarded as an unstructured isotropic dielectric, leads to the Denison–Ramsey equations

$$\Delta H_D = \frac{Ne^2}{a\varepsilon}\left(1+\frac{\partial \ln \varepsilon}{\partial \ln T}\right), \tag{4}$$

$$\Delta S_D = \frac{Ne^2}{a\varepsilon}\left(\frac{\partial \ln \varepsilon}{\partial T}\right)+\Delta S_T, \tag{5}$$

in which a is the distance between the ionic centres of the pair, while ΔS_T represents the increase in entropy due to the appearance of two species instead of one. Since the temperature coefficient $\partial \ln \epsilon/\partial \ln T$ is always negative, and for liquids exceeds unity in absolute magnitude[49], the values of ΔH_D and ΔS_D predicted by Eqns. (4) and (5) are also negative, in excellent agreement with experimental results. However, coincidence of calculated and experimental magnitudes of ΔH_D (and ΔS_D) is observed only when transition of the ions from the ion-pairs to the free state is not accompanied by changes in their solvent sheaths, i.e. usually on the dissociation of solvent-separated pairs[14,16,21,38], which provides a further test for the structure of the dissociating species.

Since the formation of solvent-separated from contact ion-pairs and that of free ions from both types are similar in character, ions being separated by one or more solvent molecules in both cases, they are governed by the same laws. For purely carbanionic systems the dissociation constant increases with decrease in the size of the cation[14,16,21,38,50] and with increase in its charge[14] (Table 2). However, the presence of a heteroatom in the organic anion reverses the dependence of the dissociation constant on the cationic radius[36,44] (Table 2). Transfer to a solvent possessing greater solvating power for the cation and a larger dielectric constant produces a sharp increase in the dissociation constant[38,42,44-46] (Table 2); it is probable that all three equilibrium constants—K_1, K_2, and K_3—increase. Solvating additives in the solution also increase the dissociation constant, of course[14,44]. In some cases[51] a linear correlation can be observed between the logarithm of the dissociation constant and the reciprocal of the dielectric constant of the medium.

Values of the dissociation constant may serve as a measure of the relative stabilities of the anions formed by dissociation[46,52]. The electron-donor character of methyl groups is responsible for the increase in K_D in the sequences of lithium derivatives (Table 2)[46]

poly-2,3-dimethylbutadienyl < polyisoprenyl < polybutadienyl,

poly-α-methylstyryl < polystyryl

Here the increase in stability of the anions is consistent with the fall in their reactivity[46,52]. However, such a rule would probably apply only to the dissociation of contact ion-pairs. The stability factor is less significant in the dissociation of solvent-separated ion-pairs (it affects, of course, the value of K_1). In any case, the dissociation constants of solvent-separated ion-pairs of lithium salts of substituted fluorenes are closely similar, although values of pK_a in the corresponding series of CH-acids vary by 4 units[37] (Table 2).

The dissociation constant of cyclopentadienyl-lithium is only around 5% of that of indenyl-lithium[46], although the pK_a of indene is 3.5 units higher[53]. Solutions of these salts, however, contain both contact and solvent-separated ion-pairs[30].

2. Aggregates of Ion-Pairs

The aggregation of ion-pairs (Eqns. 2 and 3) has been considerably less well studied than the equilibria between ions and ion-pairs or between contact and solvent-separated pairs, from both kinetic and thermodynamic points of view. Therefore the number of theoretical models created to describe these processes is also small: Fuoss and Kraus[54] examined the possibility of the formation of ion-triplets, and Pettit and Bruckenstein[55] that of symmetrical ion quadrupoles and sexapoles. The reason for the association of ion-pairs of carbanions is obviously dipole–dipole interaction, so that these aggregates are usually met in media of low polarity, such as aliphatic hydrocarbons and benzene[56,57]. Association in polar media such as oxolan is usually due to special causes, e.g. difunctionality of the polymer chain[50] or a doubly charged cation[68,69]. The stability of aggregates of ion-pairs and their degree of association depend significantly on the size of the alkali-metal cation and the structure of the anion. Polystyryl-lithium in benzene, cyclohexane, toluene, and heptane[58-60] and poly-α-methylstyryl-lithium in aliphatic hydrocarbons[63] are dimerised; polyisoprenyl-lithium in heptane, toluene, and certain other hydrocarbons forms tetramers[60-62]; and polybutadienyl-lithium[60,54] forms hexamers. On passing from this last compound to polybutadienylpotassium the degree of association of the ion-pairs falls[64] from 6 to 2. In benzene polystyrylsodium is dimerised down to concentrations of $\sim 10^{-5}$ M, dimers of potassium ion-pairs break down at $\sim 10^{-3}$ M, and caesium ion-pairs do not associate at all in this solvent[65]. In cyclohexane polystyrylpotassium is slightly associated, but the rubidium and caesium salts are monomeric[67]. Additions of solvating solvents such as oxolan tend to break down association complexes of ion-pairs in hydrocarbon media[65,66].

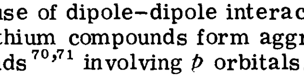
Quantitative information on the association of ion-pairs of carbanions is almost completely lacking. The equilibrium constant of the dimerisation of polystyrylpotassium is 3mM in cyclohexane at 40° C,[67] and 0.6mM in benzene at 20° C[65] ($\Delta H = 7.6$ kcal mole^{-1}).

Whereas organolithium compounds containing resonance-stabilised groups, e.g. benzyl, allyl, diphenylmethyl[56-67], associate because of dipole–dipole interaction of ion-pairs, simple alkyl-lithium compounds form aggregates with multicentre bonds[70,71] involving p orbitals. In hydrocarbons, ether, or benzene these aggregates usually comprise four[72,73] or six[74-76] monomer units. X-Ray examination indicates that tetrameric alkyl-lithium compounds have a tetrahedral structure, with lithium atoms at the corners of the tetrahedron, and alkyl groups located above the centres of the faces[72].

The association of ion-pairs of carbanions in hydrocarbons involves only the contact type. In ethers, however, solvent-separated ion-pairs also are able to associate[23]: in oxolan fluorenylsodium ion-pairs separated by a crown polyether form dimers. Increase in the dipole moment and the possibility of denser packing of ions in the dimer are probably significant here[23].

Linear carbon-chain polymers having an active centre at each end of the chain exhibit unusual behaviour. The anion formed on the dissociation of one ion-pair of difunctional polystyrylcaesium in oxolan cyclises with the ion-pair at the other end to form an intramolecular triple ion[50].

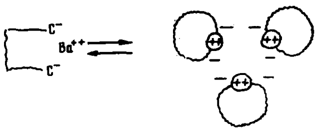
Bolaform electrolytes—caesium and sodium salts of $\alpha\omega$-difluoren-9-ylpolymethylenes



(I)
$n = 2, 3, 4$ and 6

in oxolan—form analogous triple ions[24]. The cyclisation constant increases with the number of methylene units and on passing from sodium to caesium. Formation of cyclic triple ions of sodium salts has a very low probability because the sodium cation is well solvated by oxolan.

In oxolan polystyrylbarium associates into a trimer, forming a "rosette" (**II**)[68]:



II

III. KINETIC APPROACH

The observed reaction rate constant for a compound capable of existing in more than one form is a composite quantity which, provided that the rate of establishment of equilibrium between these forms greatly exceeds the reaction velocity, can be written

$$k_{\text{obs}} = \sum_i k_i \alpha_i, \tag{6}$$

where α_i is the proportion of a given ionic species and k_i is the rate constant. Obviously, calculation of the thermodynamic activation functions from the temperature dependence of the observed rate constant may in general give incorrect results. Nor does the observed constant give a true idea of the reactivity of the ions. On the other hand, it is also clearly impossible in any case to isolate the individual rate constants k_i by means of Eqn. (6). Even in cases in which only two ionic species are in equilibrium in solution, three independent variables—the rate constants of the two species and the proportion α of one of them (the proportion of the other is $1 - \alpha$)—occur in this equation. The constants can then be determined in only one way—by varying the value of α and solving the set of linear equations

$$k_{\text{obs}} = k_1\alpha + k_2(1-\alpha) = k_2 + \alpha(k_2 - k_1). \tag{7}$$

The rate constants can also be determined graphically, by plotting k_{obs} against α, when the slope gives the difference $k_2 - k_1$, while the intercept on the ordinate axis is k_2. When these reactive species contain different numbers of ions (e.g. an ion and an ion-pair, or an ion-pair and an aggregate of ion-pairs), the quantity α can be varied by varying the concentration. When, however, the reactive species contain the same number of ions (contact and solvent-separated ion-pairs), variation of α requires the introduction of solvating additives, which displace the equilibrium towards the species having the greater interionic distance. However, this case is fraught with unpleasant consequences: firstly, free ions may be formed, i.e. yet another reactant species; and secondly, a solvent-separated ion-pair whose cation is solvated by the additive may differ in reactivity (though slightly) from an ion-pair whose cation is solvated simply by the solvent.

Obviously, it is impossible to vary the temperature or the dielectric constant of the medium, since this would entail a change in the values of the constants themselves.

Reactive systems comprising two species are among the most thoroughly studied. Many kinetic data have been assembled especially on the reactions of ionophores present in solution as an equilibrium mixture of ion-pairs and free ions. The observed rate constant for such systems can be represented by an equation suggested by Acree[77]:

$$k_{\text{obs}} = \alpha k_{\text{ion}} + (1-\alpha) k_{\text{ip}}, \tag{8}$$

where k_{ion} and k_{ip} are the reaction rate constants of ions and ion-pairs respectively, while α is the degree of dissociation calculated from conductivity data for solutions of the ionophores. In cases in which the degree of dissociation does not exceed a few percent, it can be expressed by the equation

$$K_D = \frac{C\alpha^2}{1-\alpha} \approx C\alpha^2 \ (\alpha \ll 1) \tag{9}$$

in the form $\alpha = (K_D/C)^{1/2}$, where C is the concentration of the ionophore. Formula (8) is then transformed into the very frequently used equation[36,38,42,44,50,52,78-102]

$$k_{obs} = k_{ip} + (k_{ip} - k_{ip}) \frac{K_D^{1/2}}{C^{1/2}}. \tag{10}$$

In order to evaluate k_{ip}† and k_{ion} from (10) it is sufficient to know the dissociation constant K_D. If for some reason this cannot be measured, only k_{ip} can be calculated from Eqn. (10).

The degree of dissociation α can be varied also by means of the common-ion effect, by introducing into the solution a compound that dissociates considerably better than test reagent to give one of the components (unreactive, of course) of the ion-pair. Examples of such compounds are alkali-metal tetraphenylborates[36,38,50,52], triphenylcyanoborates[42], and perchlorates[81,82]. The observed rate constant will then be given by[50,85]

$$k_{obs} = k_{ip} + (k_{ion} - k_{ip}) \frac{K_D}{[M^+]}, \tag{11}$$

where $[M^+]$ is the concentration of the common ion (in the present case the cation) calculated from the dissociation constant of the additive (since only a minute proportion of the free M^+ ions in the solution results from dissociation of the reactive ionophore). Simultaneous solution of (10) and (11) enables k_{ion}, k_{ip}, and K_D to be found without the need for conductometric measurements[38,50,82]. It is possible, of course, to use[81,82,103] Eqn. (11) independently of (10).

Table 3. Estimated contributions by free ions and ion-pairs to observed rate constant.

α	k_{ion}/k_{ip}	Contributions*, %		K_D, M	c, M	α*
		free ions	ion-pairs			
0.001	10^4	91	9	10^{-10}	10^{-5}	0.003
0.001	10^3	50	50	10^{-10}	10^{-4}	0.001
0.01	10^4	99	1	10^{-10}	10^{-3}	0.0003
0.01	10^3	91	9	10^{-8}	10^{-5}	0.03
0.01	10^2	50	50	10^{-8}	10^{-4}	0.01
0.01	10	9	91	10^{-8}	10^{-3}	0.003
0.1	10^2	91	9	10^{-6}	10^{-5}	0.4
0.1	10	53	47	10^{-6}	10^{-1}	0.003

*Approximate values.

Concluding our examination of the kinetic aspect of the joint involvement of free ions and ion-pairs in a reaction, we give some estimates‡ of the contributions by these species to the observed rate constant as functions of k_{ion}/k_{ip} and α, and for clarity values of α for certain dissociation constants and concentrations of the salt most frequently met in practice (Table 3). These data lead to further conclusions: firstly, if ions and ion-pairs differ greatly (10^3–10^4) in reactivity, ions are in effect the sole reactants, even if their proportion does not exceed 1%, a situation characteristic of the reactions of many salts whose dissociation constants exceed 10^{-8} M (e.g. Table 2); secondly, the contribution by ion-pairs becomes considerable only with a relatively small difference in reactivity between the two ionic species ($k_{ion}/k_{ip} \approx 10$) and at very low degrees of dissociation, as is typical of preparative experiments, in which large reactant concentrations are used.

Aggregates of ion-pairs make hardly any contribution to the observed rate constant, so that their role is usually merely to lower considerably the concentration of reactive ion-pairs[65,67]. If the equilibrium between the ion-pairs and their association complexes is displaced towards the latter, the observed rate constant can then be expressed[104]

$$k_{obs} = K_A^{-1/n} k_{ip} n^{-1/n} C^{1/n}, \tag{12}$$

where n is the association factor, K_A the association constant, k_{ip} the true reaction rate constant of the ion-pairs, and c the concentration of the reactant. The slope of the double logarithmic plot of observed rate constant against reactant concentration enables us to determine the association factor n and hence calculate the effective rate constant $k_{eff} = K_A^{-1/n} k_{ip}$[65,67,104]. If by varying the concentration we can bring the system into a region in which the equilibrium is completely displaced towards monomeric ion-pairs, the rate constant k_{ip} determined in this region (in which $k_{eff} = k_{obs} = k_{ip}$) enables us to calculate the equilibrium association constant K_A from k_{eff}[65,67,104].

The calculation is considerably more complicated in systems in which several reactive species are present[36,42,83,94], but this does not prevent determination of their reactivity, though less accurately.

IV. REACTIONS OF CARBANIONS

Reactions in which reactivities of carbanions have been studied, and various factors influencing them have been investigated, include nucleophilic substitution at a saturated carbon atom (alkylation of carbanions), nucleophilic addition (mainly polymerisation of vinyl monomers), and processes involving proton and electron transfer. These four types of reactions will be discussed below.

1. Nucleophilic Substitution

The reactivity of carbanions in nucleophilic substitutions has been studied only on the fluorenyl system (9-RFl^-M^+)[36,37,45,78-82,105]. However, such restriction to a single hydrocarbon has not prevented (and may have helped) establishment of the effects on reactivity of the most diverse

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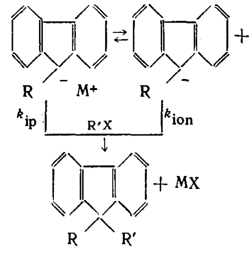
† The value of k_{ip} obtained from the intercept relates to all types of ion-pairs present together in the solution: i.e. it can be written in the form (6), where k_i will represent the reactivity of the ith kind of ion-pairs.

‡ These estimates are valid for any pair of ionic species in equilibrium, e.g. for contact and solvent-separated ion-pairs. The only difference is that the calculation of α requires that Eqn. (9) should be replaced by a different formula, representing the given type of equilibrium.

factors—substituents at the anionic centre, the size of the alkali-metal cation, the nature of alkylating and leaving groups, the character of the solvent. The general scheme of the reactions appeared to be



(13)

where R = H, CH_3, C_6H_5,[37,79] $SO_2C_6H_5$,[81,82] $COOCH_3$,[37,81,82] and CN[36,37,45,78,80–82,105]; $M^+ = Li^+, Na^+, K^+, Cs^+, (C_6H_5)_4 . As^+$; R' = CH_3, C_2H_5, C_3H_7, iso-C_3H_7, C_4H_9,[36,45,78,80,105] *m*- and *p*-substituted $C_6H_5CH_2$;[105] and X = F, Cl, Br, I. The solvents used comprised alcohols, dipolar aprotic solvents, and solvents of ether type. The principal results obtained in these investigations are summarised in Tables 4–7.

Table 4. Kinetic parameters of the reaction of alkali-metal salts of 9-cyanofluorene (9-$CNFl^-M^+$) with alkyl halides (RX) at 25° C.

M	Solvent	RX	10^3k_{ip}, $M^{-1}\,s^{-1}$	10^3k_{ion}, $M^{-1}\,s^{-1}$	k_{ion}/k_{ip}	$\Delta H^{\neq}$, kcal mole^{-1}	$\Delta S^{\neq}$, e.u.	Ref.
Li	DME	MeI	3.6	1750	485	—	—	36
Li	DME	EtI	2.8	81	29	—	—	36
Li	DME	PrI	1.6	28	18	—	—	36
Li	DME	PrBr	0.34	18	53	—	—	36
Li	DME	BuBr	0.019	2.7	142	—	—	36
Na	ethanol	MeI	—	144*	—	13.3	—18.7	105
Na	DME	MeI	39	1620	42	—	—	36
Na	DME	EtI	8	60	8	—	—	36, 78, 80
Na	HMPA	EtI	—	78	—	—	—	45
Na	DMAA**	EtI	—	68	—	—	—	45
Na	DMFA***	EtI	—	66	—	—	—	45
Na	DMSO****	EtI	—	48	—	—	—	45
Na	AN*****	EtI	—	20	—	—	—	45
Na	ethanol	EtI	—	13.1	—	—	—	45, 80
Na	ethanol	EtI	—	22.3*	—	14.1	—19.6	105
Na	ethanol	iso-PrI	—	8.84*	—	13.7	—22.7	105
Na	ethanol	iso-PrBr	—	2.31*	—	22.0	1.8	105
Cs	DME	EtI	11	93	11	—	—	36

*At 30.5° C.
**Dimethylacetamide.
***Dimethylformamide.
****Dimethyl sulphoxide.
*****Acetonitrile.

In all cases association of the carbanion with the cation deactivates the nucleophile: with one exception (the reaction of 9-cyanofluoren-9-ylsodium with benzyl fluoride[81,82]—Table 5) the rate constant of the free ion exceeds that of the ion-pair: i.e. $k_{ion}/k_{ip} > 1$. This was to be expected, since the activated complex formed in the reaction of the ion-pair (III) differs from that for reaction of the free carbanion (IV) (coordination of the cation M^+ with the leaving group X^- in the transition state is a special case):

$$M^+C^- \rightarrow M^+C^{\delta-} \ldots C^{\delta+} \ldots X^{\delta-} \quad C^- \rightarrow C^{\delta-} \ldots C^{\delta+} \ldots X^{\delta-}$$

(III) (IV)

The presence of the cation in (III) tends to localise the charge on the carbanion, which prevents formation of a new ethylenic bond or else increases the effective distance between the charged centres of the anion, thereby weakening the Coulombic interaction of the reactants.

Table 5. Kinetic parameters of the reactions of benzyl halides $C_6H_5CH_2X$ with alkali-metal salts of 9-substituted fluorenes (9-RFl^-M^+) in alcohols at 30° C.

X	R	M+	Solvent	k_{ip}, $M^{-1}\,s^{-1}$	k_{ion}, $M^{-1}\,s^{-1}$	k_{ion}/k_{ip}	Ref.
F	CN	Na	t-BuOH	$\sim1.9\cdot10^{-3}$	$\sim1.9\cdot10^{-3}$	~1	81, 82
F	SO_2Ph	Na	t-BuOH	$\sim2\cdot10^{-3}$*	—	—	81
Cl	COOMe	Li	t-BuOH	0.185	4.27	23	81
Cl	COOMe	Na	t-BuOH	0.124	4.27	34	81
Cl	CN	Na	t-BuOH	0.20	4.1	20.5	81, 82
Cl	CN	Na	EtOH	—	0,127	—	105
Cl	COOMe	K	t-BuOH	0.097	4.27	44	81
Cl	SO_2Ph	Na	t-BuOH	~0.2*	—	—	81
Br	CN	Na	EtOH	—	6.79**	—	105
Br	CN	Na	t-BuOH	11	350	32	81, 82
Br	COOMe	Na	t-BuOH	7.76	256	33	81
Br	COOMe	K	t-BuOH	3.88	256	66	81
Br	SO_2Ph	Na	t-BuOH	~7*	—	—	—

*Observed reaction rate constant.
**At 25° C.

Table 6. Rate constants for the reactions of sodium 9-cyanofluoren-9-ide with substituted benzyl halides $YC_6H_4CH_2X$ in ethanol[105].

Y	10^2k_{ion}, $M^{-1}\,s^{-1}$		Y	10^2k_{ion}, $M^{-1}\,s^{-1}$	
	X=Br (10° C)	X=Cl (20° C)		X=Br (10° C)	X=Cl (20° C)
H	295	6.46	3-Cl	611	13.7
3-Me	527	11.9	3-Br	707	—
4-MeO	808	11.9	3-NO_2	3040	55.3
3-MeO	—	8.96			

Table 7. Influence of structure of carbanion on its reactivity during alkylation and benzylation.

System	R	10^8K_D, M	k_{ion}, $M^{-1}\,s^{-1}$	k_{ip}, $M^{-1}\,s^{-1}$	k_{ion}/k_{ip}	pK_a*
9-RFl^-Li^+ + BuBr (DME, 25°) (Ref.37)	CN	30.1	$2.7\cdot10^{-3}$	$1.9\cdot10^{-5}$	142	8.6[37]
	COOMe	6.6	$6.7\cdot10^{-3}$	$1.0\cdot10^{-4}$	67	10.3[106]
	Ph	560	$2.2\cdot10^{-1}$	$7.4\cdot10^{-2}$	3	16.4[106]
	Me	380	20.2	6.3	3.2	19.7[106]
	H	470	21,6	9.9	2.2	20.5[106]
9-RFl^-Na^+ + $C_6H_5CH_2Cl$ (t-C_4H_9OH, 30° C) (Refs.81,82)	CN	810	4,1	0.20	20.5	11,4[108]
	COOMe	130	4.27	0.124	34	12.9[108]
	SO_2Ph	35	—	~0.2**	—	15.0[81]
9-RFl^-Na^+ + $C_6H_5CH_2Br$ (t-C_4H_9OH, 30° C) (Refs.81,82)	CN	810	350	11	32	11.4[108]
	COOMe	130	256	7.76	33	12.9[108]
	SO_2Ph	35	—	~7**	—	15.0[81]

*These values of pK_a were used in discussing the results in the papers cited.
**Observed reaction rate constant.

Hence the ratio k_{ion}/k_{ip} for a fixed anion structure should increase with the interaction between the ionic moieties of the pair. For contact ion-pairs the ratio may be expected to increase in the sequence $Cs^+ < K^+ < Na^+ <$

Li^+. On the other hand, on passing from contact to solvent-separated ion-pairs, in which the oppositely charged components are a long distance apart, the relative reactivity of the carbanion should decrease considerably. This is indeed the case: in the reactions of the lithium salts of fluorene and of its 9-methyl and 9-phenyl derivatives in dimethoxyethane solution, where their ion-pairs are separated by the solvent, the ratio is only $k_{ion}/k_{ip} = 2$–3[37] (Table 7).

The dependence of the ratio on the size of the cation is different in dimethoxyethane from that in t-butyl alcohol: in the ether the reactivity of the ion-pairs increases in the sequence $Li^+ < Na^+ < Cs^+$[36] (Table 4), but in the alcohol in the sequence $K^+ < Na^+ < Li^+$[81] (Table 5). However, although it can be accepted[36] that contact ion-pairs are present in dimethoxyethane, the situation in t-butyl alcohol is not altogether clear. In any case, this question has not been specially investigated[81], and the possibility of the solvation of ambident anions (as is the anion of methyl fluorene-9-carboxylate) by hydrogen bonding[107] does not exclude the presence of solvate-separated ion-pairs in solutions of the alkali-metal derivatives of this ester.

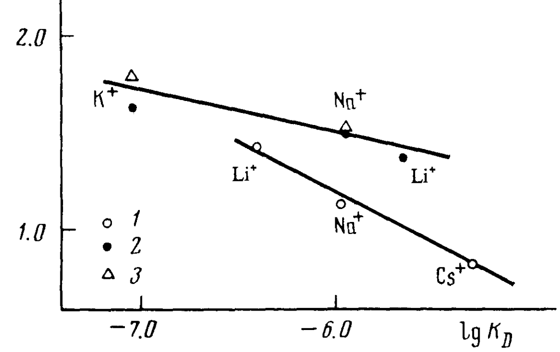


Figure 1. Correlation of relative reactivity of carbanion with dissociation constants of its ion-pairs (Tables 4 and 5): 1) C_2H_5I; 2) $C_6H_5CH_2Cl$; 3) $C_6H_5CH_2Br$.

Nevertheless, the variation of the ratio in one or other system can be predicted from the dissociation constant of the ion-pairs, the parameter which ultimately characterises their stability. Fig. 1 shows double logarithmic graphs of the dependence of k_{ion}/k_{ip} on K_D based on data obtained for the benzylation of alkali-metal salts of methyl fluorene-9-carboxylate with benzyl chloride and bromide in t-butyl alcohol and for the alkylation[36] of alkali-metal salts of 9-cyanofluorene with ethyl iodide in dimethoxyethane. In the latter case the mean value for the three salts investigated $k_{ion} = 0.078\ M^{-1}\ s^{-1}$ was used for the correlation, with a correction for the involvement of the sodium salt of solvent-separated ion-pairs[80]. The linearity of the graphs indicates the existence for these systems of a free-energy relation of the type

$$\lg \frac{k_{ion}}{k_{ip}} = A + B \lg K_D , \qquad (14)$$

while the negative slopes suggest that the reactivity of an ion-pair decreases with increase in the interaction between its components, as had been postulated for the transition state (III). Results for the action of benzyl chloride and bromide on alkali-metal salts of methyl fluorene-9-carboxylate lie on the same graph, which indicates a parallel variation in the reactivity of ions and ion-pairs in both processes. A relation of type (14) is satisfied for certain other nucleophilic substitutions[94].

A formal kinetic interpretation of the reactivity of the anion, with the aim of explaining why it may exceed considerably that of ion-pairs in the benzylation of alkali-metal salts of 9-substituted fluorenes, but also may have the same activity ($k_{ion}/k_{ip} \approx 1$), has been based[81,82] on the scheme

$$\begin{tikzcd}
M^+C^- + RX \arrow[r, shift left, "k^1_{ip}"] \arrow[d, shift right, "K_D"'] & (\text{Complex})_1 \arrow[l, shift left, "k^{-1}_{ip}"] \arrow[r, "k^2_{ip}"] & CR + MX , \\
M^+ + C^- + RX \arrow[u, shift right] \arrow[r, shift left, "k^1_{ion}"] & (\text{Complex})_2 \arrow[l, shift left, "k^{-1}_{ion}"] \arrow[r, "k^2_{ion}"] & CR + MX .
\end{tikzcd} \qquad (15)$$

With reversible formation of intermediate complexes, which can be termed specific solvation of one reactant by the other or e.g. coordination of the cation by the leaving group, k_{ip} and k_{ion} will actually become respectively $k^1_{ip}k^2_{ip}/(k^{-1}_{ip} + k^2_{ip})$ and $k^1_{ion}k^2_{ion}/(k^{-1}_{ion} + k^2_{ion})$. It is clear that, with operation of the mechanism (15), the ratio k_{ion}/k_{ip} will be determined by the relations between the rate constants of the individual stages; it can vary within wide limits, and be either greater or less than unity.

The influence of the medium on the reactivity of the 9-cyanofluoren-9-ide anion can be traced in its reactions with ethyl iodide[45,80,105] (Table 4) and with benzyl halides[81,82,105] (Table 5). A distinguishing feature of the first reaction is the absence of a clear effect of the dielectric constant, which is typical of nucleophilic substitution[109]. Thus the rate constant has the same value in dimethoxyethane and in hexamethylphosphoramide ($\epsilon = 7.2$ and 30 respectively[110]); on the other hand, it decreases on passing from dimethylacetamide, dimethylformamide, and acetonitrile to ethanol (37.8, 36.7, 37.5, and 24.5[110]). This type of effect of the medium is usually interpreted in terms of the degree of solvation of the reactants and the activated complex[109].

Since the rate constant for the reaction of the 9-cyanofluoren-9-ide anion with ethyl iodide falls in parallel with the shift of the absorption band maxima of the anion to shorter wavelengths[45], it can reasonably be assumed that the factor determining the reactivity of a nucleophile is its degree of solvation. The observed sequence of variation in the solvating power of solvents

DME ≈ HMPA < DMAA < DMFA < DMSO < ethanol

characterises the solvation of the most diverse anions[109], both typically "hard" (Cl^-, N_3^-, CN^-, Br^-) and typically "soft" (SCN^-, I^-). Increase in the solvating power of dipolar aprotic solvents for these species is accompanied by decrease in the logarithm of the activity coefficients of the anions $\lg\gamma_{Y^-}$, the variation in the logarithm for each anion being almost the same in character despite the difference in absolute magnitude[109]. This enables us to compare the reactivity of the 9-cyanofluoren-9-ide anion with the logarithm for other anions (Fig. 2). In the present case we have used values of $\lg\gamma_{Y^-}$ for the thiocyanate ion, which probably resembles the 9-cyanofluoren-9-ide anion in softness, although analogous correlations exist with the logarithm for other anions. The linear dependence of

$2 + \lg k_{\mathrm{ion}}$ on $\lg \gamma_{\mathrm{SCN^-}}$ for four solvents (Fig. 2) is a further confirmation of the dominant role of solvation particularly of the anion. The misplacement of the point for acetonitrile is probably due to some specific effects of solvation of the activated complex.

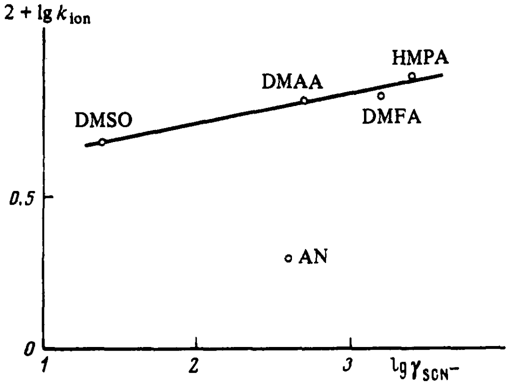


Figure 2. Correlation of reactivity of 9-cyanofluoren-9-ide anion with activity coefficients $\lg \gamma_{\mathrm{SCN^-}}$ in a series of dipolar aprotic solvents.

The rate constant k_{ion} for the reaction with ethyl iodide decreases by a factor of 6 on passing from dimethoxyethane to ethanol (Table 4). The effect of the solvent is considerably stronger in the reactions with benzyl halides: the ratio of the rate constant in t-butyl alcohol to that in ethanol is respectively 32 and ~ 50 for benzyl chloride and bromide (Table 5). Operative factors here are probably the lower solvating power of the higher alcohol and its lower dielectric constant (11.2 and 24.5[110]). It is also possible that the activated complex is differently solvated by alcohols in the reactions of the anion with benzyl halides and with primary alkyl halides[109].

The reactivity of a carbanion (indeed of any other species) depends mainly on its stability, which may be measured by the pK_a of the original CH-acid. Apart from this, we can compare the actual rate constants of the carbanion with dissociation constants of its ion-pairs[46,52] and also with its anodic oxidation potential[111]. In reactions of anions of 9-substituted fluorenes with butyl bromide in dimethoxyethane the rate constant k_{ion} increases as the hydrocarbon becomes less acidic (Table 7), while the graph of the dependence of $\lg k_{\mathrm{ion}}$ on pK_a is a straight line of slope 0.35.[37] The rate constant increases also with decrease in the dissociation constant of contact ion-pairs (lithium salts of 9-cyanofluorene and methyl fluorene-9-carboxylate—Table 7). In reactions with benzyl halides (Table 7), however, change in the character of the substituent at the anionic centre has hardly any effect on the reactivity of the nucleophile[81,82]. This was explained[81] in terms of the transition state, in which rupture of the carbon–halogen bond occurred to a considerably greater extent than formation of a new carbon–carbon bond. However, these deductions are in no way supported by kinetic data.

On the other hand, the increase in the rate constant for reaction of the 9-cyanofluoren-9-ide anion with benzyl chloride and bromide, on the introduction of electron-donor and electron-acceptor substituents in *meta*- and *para*-positions[105] (Table 6), presupposes synchronous rupture of the old bond and formation of the new. In this case the transition state is stabilised both by acceptors (which increase the degree of rupture of the carbon–halogen bond in comparison with the degree of formation of the carbon–carbon bond) and by donors (which increase the degree of formation of the new bond in comparison with the degree of rupture of the old bond)[105]. This transition state corresponds to a mechanism of nucleophilic substitution intermediate between S_N1 and S_N2. This would be supported by the absence of a first-order reaction with respect to the electrophilic reagent, but measurements were made[105] at only one concentration of the benzyl halide.

Reaction velocities both of free anions and of their ion-pairs are strongly dependent on the character of the leaving group and on the alkyl group. The general rules are the same for alcohols and for dimethoxyethane: $F < Cl < Br$[81,82]; $Cl < Br < I$[36,105]; $C_6H_5CH_2 \gg CH_3 > C_2H_5 > \text{iso-}C_3H_7 > \text{t-}C_4H_9$;[105] and $CH_3 > C_2H_5 > C_3H_7 > C_4H_9$.[36] Thus the rate increases as the carbon–halogen bond becomes weaker and decreases with diminution in the effective positive charge on the α carbon atom and with intensification of the steric hindrance to attack by the nucleophile due to introduction of α-alkyl groups. Variations in $k_{\mathrm{ion}}/k_{\mathrm{ip}}$ in the reactions of carbanions and their ion-pairs are usually successfully interpreted[36,105] in terms of Pearson's principle[112] of hard and soft acids and bases.

2. Proton Transfer

Very great interest has been taken in proton-transfer reactions, so that many researches have been undertaken on them. We shall consider firstly studies in which the nature of the reactant species has been accurately established, and quantitative information obtained on their reactivity. We note at once that available data are largely contradictory, and the general picture is by no means clear.

Table 8. Rate constants for the reactions of polystyrylsodium and -potassium with triphenylmethane[38] at 25° C.

Cation	Solvent	k_{ion}, $M^{-1}\,s^{-1}$	k_{ip}, $M^{-1}\,s^{-1}$	$\frac{k_{\mathrm{ion}}}{k_{\mathrm{ip}}}$
Na^+	oxolan	178	0.15	1190
Na^+	DME	138	11	12.5
K^+	oxolan	142	<0.2	>710

Smid has investigated several proton-transfer reactions in which CH-acids act as donors, and alkali-metal salts of such acids as acceptors[17,38,113]. In the reactions of triphenylmethane with polystyrylsodium in oxolan and dimethoxyethane and with polystyrylpotassium in oxolan[38] the free anions possess the greatest reactivity, with closely similar rate constants in the two solvents (Table 8).

Since k_{ip} cannot be determined accurately, it is difficult to know how the cation influences the reactivity of the ion-pairs. On the other hand, the considerable increase in k_{ip} on passing from oxolan to dimethoxyethane suggests that solvent-separated are more active than contact ion-pairs, since the proportion of the latter is considerably higher in dimethoxyethane[43,83]. Thus the reactivity of the ionic species of "living" polystyrene towards triphenylmethane increases in the sequence from the contact to the solvent-separated ion-pair and then to the free carbanion.

Investigations on the reactions of the lithium, sodium, caesium, and tetrabutylammonium salts of fluorene with 1,2- and 3,4-benzofluorenes in oxolan, dimethoxyethane, and dioxan were more qualitative in character[17]. In almost all cases the observed rate constant increases with the concentration of the fluorenide, which would appear to prove that the free fluorenide anion is the most reactive. However, this increase is considerably larger than is to be expected for a mechanism of simultaneous involvement of ions and ion-pairs in the reaction. Thus for the reaction of fluorenyl-lithium with 3,4-benzofluorene in oxolan the constant increases by a factor of 60 when the concentration of the lithium salt is diminished by a factor of 260,[17] although at most a 16-fold increase would have been expected. In the reaction of 1,2-benzofluorene with the sodium salt of fluorene in dioxan the constant increases by a factor of 23 when the concentration of the salt decreases by a factor of 35.

The results were explained[17] on the hypothesis that ion-pairs of fluorenyl-lithium and fluorenylsodium associate, with possible formation in dioxan of aggregates of five ion-pairs, although this postulate is inconsistent with these workers' own conductivity measurements on the salts[11,15,16]. In the reaction of the caesium salt of fluorene with 1,2-benzofluorene in oxolan and dioxan the rate constant increases very moderately with dilution, which is consistent with the simultaneous participation of ions and ion-pairs in detaching the proton[17]. In this case the caesium contact ion-pair is less reactive than the fluorenide anion. A solvent-separated ion-pair may be either more or less reactive than a contact ion-pair depending on the solvent (dimethoxyethane or oxolan)[17].

There are many obscurities also in an investigation[114] on the protonation of the lithium and sodium salts of 1,3-diphenylpropene by fluorene in oxolan, 2,5-dimethyloxolan, and 2,3-dihydropyran. In oxolan the sodium salt has almost thousandfold the activity of the lithium salt. In this solvent 1,3-diphenylallyl-lithium comprises solely solvent-separated ion-pairs, whereas 1,3-diphenylallylsodium is a mixture of loose and intimate ion-pairs. From this it was concluded that contact ion-pairs are considerably more reactive[114]. On the other hand, in 2,5-dimethyloxolan, in which both salts are present only as contact ion-pairs, the difference in reactivity reaches a factor of almost 10^5: the rate constants at 23°C are respectively ~ 0.002 and 195 M^{-1} s^{-1} for lithium and sodium. No allowance was made for the role of free ions (although measurements were made at concentrations of 10^{-4}–10^{-3}M) or association complexes of ion-pairs of 1,3-diphenylallyl-lithium, whose formation is very likely in this system. The exotic structure suggested[114] for the intermediate complex is frankly speculative.

In spite of some uncertainty in the reactivities of the ionic species, the results obtained by Smid[17,38,113] indicate that the rate constant for proton transfer from a CH-acid to a carbanion is independent of the difference in pK_a between the donor and the conjugate CH-acid of the carbanion. In the reaction of the polystyryl anion with triphenylmethane in oxolan we have[38] $k_{ion} \approx 150\,M^{-1}\,s^{-1}$ with $\Delta pK_a \approx 3.5$. On the abstraction of a proton by the fluorenide anion from 9-methylfluorene under the same conditions[38] $k_{ion} \approx 100\,M^{-1}\,s^{-1}$ with $\Delta pK_a \approx 0$. Less obviously the observed rate constants[38] for protonation of the dianion of 1,1-diphenylethylene by 9-propylfluorene ($\Delta pK_a \approx 10$) and of fluorenylsodium by 1,2-benzofluorene (~ 2) are approximately 20 and 10^3 M^{-1} s^{-1} (in oxolan at 25°C).

A similar conclusion was reached by Ritchie[115], who investigated proton transfer between CH-acids and carbanions in dimethyl sulphoxide[115-118]. In this solvent alkali-metal salts of CH-acids are probably completely dissociated at low concentrations, so that the observed rate constants can be regarded as those of the free carbanions. At high concentrations of the salts, however, ionic association begins to influence the rate of proton transfer. Thus for fluorene and fluorenyl-lithium in dimethyl sulphoxide at 25°C at a salt concentration of ~ 0.5M the proton-exchange rate constant is ~ 0.5 M^{-1} s^{-1}.[119] Yet the rate constants for proton transfer between substituted fluorenes and their carbanions at concentrations of $\sim 10^{-4}$M vary over the range 10^3–10^4 M^{-1} s^{-1}.[116-118] It is quite possible that not only ion-pairs but also their aggregates are present at high concentrations of fluorenyl salts even in such a polar solvent as dimethyl sulphoxide.

Association plays an especially important part in the reactions of alkyl-lithium compounds. In the metallation of triphenylmethane in oxolan the reactivity of the lithium alkyls is determined not by their basicity or the acidity of the original CH-acids but by the stability of the aggregates[120,121]. With the concentration of the alkyl-lithium compound 0.1M the relative metallation rate constant increases in the sequence from methyl (1.0), vinyl (4.2), phenyl (6.3), n-butyl (23), allyl (90), to benzyl (450); the corresponding sequence at 0.01M concentration increases from methyl (1.0), phenyl (2.8), vinyl (4.3), allyl (14), n-butyl (20), to benzyl (150).

Table 9. Kinetic parameters[122,123] of the protonation of the benzyl anion and its ion-pairs in oxolan at 24°C.

Donor	Cation	$10^{-8}k_{ion}$, M^{-1} s^{-1}	$10^{-8}k_{ip}$, M^{-1} s^{-1}	$\frac{k_{ip}}{k_{ion}}$
H_2O	Na^+	0.53	55	104
MeOH	Li^+	2.3	3.4	1.5
MeOH	Na^+	2.3	58	25
MeOH	Bu_4N^+	2.3	6.0	2.6
EtOH	Na^+	1.4	37	26
EtOD	Na^+	1.2	21	17.5
t-BuOH	Li^+	0.16	9.7	61
t-BuOH	Na^+	0.16	13	81
t-BuOH	Bu_4N^+	0.16	4.6	29

The technique of pulsed radiolysis[122,123] has enabled rate constants to be determined for the very fast reactions involving protonation of the benzyl anion and its anion-pairs by various proton-donor compounds in oxolan. Benzyl anions were formed on the irradiation of solutions containing dibenzylmercury; in the presence of sodium tetraphenylborate[122] or of lithium or tetrabutylammonium perchlorate[123] their cations combine rapidly (in the case of the sodium ion the rate constant is 1.5×10^{11} M^{-1} s^{-1}) with benzyl anions to form the corresponding ion-pairs. Whether or not these salts are present the solutions contain only one ionic species, which facilitates considerably analysis of the kinetic data.

The results are quite remarkable (Table 9). Firstly, the reactivity of the ionic species increases with the acidity of the alcohol (definite rules of this type are not found in protonations involving CH-acids as donors[38,115-118]). Secondly, the rate constants for protonation of the carbanion are far smaller than the values typical of diffusion-limited processes (e.g. for detachment of a proton by the conjugate bases of NH- and OH-acids[124]). Finally, the most interesting result is that ion-pairs are considerably more active than the free carbanions. The explanation advanced[122] for this last fact was that a transition from the delocalised (benzyl) anion to an anion having a very high degree of localisation of negative charge (an oxo-anion, RO^-) takes place during the reaction. The activated complex, which will be characterised by greater charge localisation than in the original carbanion because of the involvement of an oxygen atom donating a proton, should be more stable in the presence of a cation because of the Coulombic interaction energy. From this point of view stabilisation of the activated complex by the cation would not be expected during protonation of carbanions by CH-acids, which is consistent with Smid's observations[38].

When the stability of the benzyl type of anion is enhanced, e.g. by the introduction of electron-accepting substituents into the ring, the rate constants for protonation by water and alcohols decrease[125]. Thus k_{ion} for the reaction of $C_6F_5CH_2^-$ with water and methanol in oxolan is respectively 3.3×10^6 and 1.2×10^6 M^{-1} s^{-1}. In this case, however, not only does the absolute reactivity of the carbanion decrease but the relative reactivities of the ionic species are reversed. The sodium ion-pair of the perfluorinated benzyl anion reacts at little more than one-tenth of the speed of the carbanion $k_{ip} = 4.3 \times 10^5$ M^{-1} s^{-1}. The results obtained are not yet sufficient to explain the divergence from the results for protonation of the unsubstituted benzyl anion[122,123].

The stereochemistry of protonation may provide information on the nature of the reactant species. Thus in the protonation[126] of the lithium and sodium salts of 9,10-dialkyl-9,10-dihydroanthracene in ether, oxolan, and hexamethylphosphoramide contact ion-pairs give a *cis*-product, whereas loose ion-pairs and free carbanions yield a *trans*-product.

3. Electron Transfer

Although the oxidation of carbanions is quite widely used for preparative purposes[127,128], hardly any kinetic study has been made of these processes. Quantitative information on the reactivity of ions and ion-pairs has been obtained only for oxidation of the sodium salts of 9-substituted fluorenes (with cyano, methoxycarbonyl, benzoyl, methylsulphonyl, phenylsulphonyl as substituent) by molecular oxygen in t-butyl alcohol and its mixtures with dimethyl sulphoxide[82,103,129], in which fluorenone is formed in at least 85% yield independently of the nature of the substituent. Even in this case, however, the kinetic parameters (Table 10) cannot be regarded as absolutely reliable, since corrections could not be made for salt effects due to sodium perchlorate and tetraphenylborate added§ to the reaction medium. The absence of a dependence of k_{ion} and k_{ip} on the stability of the carbanions (which may be measured by the pK_a of the original [substituted] hydrocarbon—CN 11.4,[108] $COOCH_3$ 12.9,[108] $SO_2C_6H_5$ 15.0[81]), as well as the variation of the ratio k_{ion}/k_{ip} from values exceeding unity ($R = SO_2C_6H_5$) to values less than unity (R = CN), suggests a mechanism of type (15).[82] As a consequence of the formation of an unstable intermediate product (though of unknown structure) in the oxidation of sodium methoxycarbonylfluoren-9-ide, the rate of appearance of fluorenone is only 2% of the rate of consumption of the salt[82]. The greater reactivity of the ion-pair than of the carbanion may be due[82] to involvement of the cation in stabilising the transition state (R = CN), although this may be hindered by bulky substituents at the reaction centre ($R = SO_2C_6H_5$).

Table 10. Kinetic parameters[82,103] of the oxidation by molecular oxygen of the sodium salts of 9-substituted fluorenes (9-RFl^-Na^+) at 30°C.

Solvent	R	10^4k_{ip}, s^{-1}	10^4k_{ion}, s^{-1}	$\frac{k_{ion}}{k_{ip}}$
$t\text{-}C_4H_9OH$	CN	83	60	0.72
$t\text{-}C_4H_9OH$	COOMe	160	—	~1
$t\text{-}C_4H_9OH$	SO_2Ph	0.75	13	17.3
$t\text{-}C_4H_9OH$ + 1 M DMSO	CN	3.73	0.69	0.185
$t\text{-}C_4H_9OH$ + 1 M DMSO	SO_2Ph	0.195	1.34	6.9

The rate of oxidation of the 2-phenyldibiphenyleneallyl carbanion by molecular oxygen is greatly influenced[130] by the form in which the ion exists in solution (free or paired with an alkali-metal cation). The increase in the relative rate of oxidation in the sequence from dimethyl sulphoxide and dimethylformamide (1), pyridine (50), dimethoxyethane (~ 570), oxolan (2100), 2-methyloxolan (50 000), to diethyl and di-n-butyl ethers (> 10^5), i.e. with decrease in dielectric constant and solvating power, suggests that the most reactive species is the contact ion-pair.

In the oxidation by molecular oxygen of the triphenylmethyl anion[131,132], formed in small quantities in the presence of alkali-metal hydroxides or alkoxides, however, ion-pairs probably possess insignificant activity. In any case this provides an interpretation of the increase in the relative reaction velocity in the sequence[131] from t-butyl alcohol (< 1) through 80% pyridine–t-butyl alcohol (2), 80% dimethylformamide–t-butyl alcohol (39), 80% dimethyl sulphoxide–t-butyl alcohol (110), and 80% hexamethylphosphoramide–t-butyl alcohol (128) to hexamethylphosphoramide (> 230) or the acceleration of the process by additions of dicyclohexyl-18-crown-6.[132] Similarly, the rate of oxidation of 9-phenylfluorene, 9-methylfluorene, and 1,1-diphenylethane in the presence of potassium t-butoxide increases on passing from t-butyl alcohol to hexamethylphosphoramide[131]. It is interesting, however, that, when nitrobenzene is used as oxidant[132], the ion-pairs of the triphenylmethyl anion become more reactive than the free carbanion.

The oxidation by aromatic nitro-compounds (nitrobenzene, *m*-dinitrobenzene, *p*-nitrobenzonitrile, and 1,3,5-dichloronitrobenzene) of anions of 9-substituted fluorenes[133,134] (with methoxyl, methyl, isopropyl, amino, and

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§ For the determination[82,103] of reaction rate constants of ions and ion-pairs the degree of dissociation of the sodium salts was varied by adding the perchlorate and the tetraphenylborate: i.e. the calculations were based on an equation of type (11).

hydroxyl as substituent), formed in the presence of alkali-metal and tetra-alkylammonium methoxides in methanol, is represented by the scheme

$$\begin{gathered} RH + B^- \rightleftarrows R^- + BH, \\ R^- + PhNO_2 \rightrightarrows R^\cdot + PhNO_2^{\dot{-}}, \\ R^\cdot \rightarrow {}^1/_2\,R{-}R, \\ PhNO_2^{\dot{-}} \rightarrow {}^2/_3\,PhNO_2 + {}^1/_2\,PhNO^{\dot{-}}, \\ PhNO^{\dot{-}} + R^\cdot \rightarrow \text{Nitrone}. \end{gathered} \qquad (16)$$

The complicated mechanism prevents determination of rate constants for individual stages. The rate of consumption of 9-methoxyfluorene in the presence of nitrobenzene decreases[134] in the sequence of methoxides

potassium > tetramethylammonium ≈ lithium.

4. Nucleophilic Addition

Quantitative information on the reactivity of the carbanions and their ion-pairs has been obtained for addition to a double bond[42,43,50,65,67,68,82-102,135,136] and for the cleavage of cyclic oxides of alkenes[33,137,138]. Current views on the influence of various factors on the kinetics and the mechanism of reactions involving carbanionic species are based primarily on results obtained by Szwarc and his coworkers[85-88] in an investigation of the anionic polymerisation of vinyl monomers, i.e. addition to a double bond. We shall consider only the main rules characterising these processes.

Table 11. Reaction rate constants of free ions and ion-pairs in the anionic polymerisation of alkenes at 25° C.

Anion*	Solvent	k_{ip}, $M^{-1}\,s^{-1}$					k_{ion}, $M^{-1}\,s^{-1}$	Ref.
		Li^+	Na^+	K^+	Rb^+	Cs^+		
Polystyryl	cyclohexane	—	—	7.7	22.5	19	—	67
Polystyryl	benzene	—	—	47	24	18	—	65
Polystyryl	dioxan	0.9	3.4	20	21.5	24.6	—	139
Polystyryl	oxan**	19.5	17.5	30	40	—	130 000	140
Polystyryl	oxolan	160	80	~50	~50	~22	65 000	50
Polystyryl	DME	—	3600	—	—	150	40 000	83
Poly-*p*-methoxystyryl	oxolan	—	40	40	—	25	40 000	89
Poly-*o*-methylstyryl	2-methyloxolan	2	1	16	—	30	20 000	90
Poly-α-methylstyryl	dioxan	—	0.02	0.1	0.06	—	—	91
Poly-α-methylstyryl	oxan	2.6	0.047	0.25	0.26	0,26	830	91
Polyisoprenyl	oxan**	0.20	—	—	—	—	2 800	92

*The polystyryl, poly-*p*-methoxystyryl, poly-*o*-methylstyryl, poly-α-methylstyryl, and polyisoprenyl anions react respectively with styrene, *p*-methoxystyrene, *o*-methylstyrene, α-methylstyrene, and isoprene.

**Measurements made at 30° C.

Addition of an alkene molecule to an active chain-growth centre leads every time to reproduction of the centre, so that we can regard anionic polymerisation of an alkene (neglecting effects of the polymer chain, which have little significance in the formation of a carbon-chain polymer[85]) simply as a reaction of the type

$$\geqslant C^-M^+ + \rangle C{=}C\langle \;\rightarrow\; \geqslant C^-M^+, \qquad (17)$$

where $\geqslant C^-M^+$ denotes an alkali-metal salt of a CH-acid capable of reacting either as a free ion, an ion-pair, or any other more complicated ionic species (Eqns. 1–3). Table 11 gives the most characteristic rate constants k_{ion} and k_{ip} obtained for the polymerisation of vinyl monomers (more complete information can be obtained from the above references).

The anionic polymerisation of alkenes is characterised by large differences in reactivity between free carbanions and contact ion-pairs: in solvents in which few if any solvate-separated ion-pairs are present (dioxan, oxolan, oxan, 2-methyloxolan) k_{ion} exceeds k_{ip} by factors of 10^3–10^4 (Table 11). On passing to solvents possessing a high solvating power for alkali-metal cations (dimethoxyethane, glymes), however, values of k_{ip} increase sharply[89,93], because of the higher proportion of solvent-separated ion-pairs, whose reactivity is as much as 30–50% of that of the free carbanions[42,43,83].

The presence of both loose and close ion-pairs in solution sometimes leads to an anomalous temperature variation of k_{ip}. Thus lowering the temperature from 50 to 0° C leads to an increase in k_{ip} for the reaction of polystyrylsodium with styrene in dimethoxyethane[83], and only at lower temperatures does the activation energy acquire the normal positive value. This is because the activation energy E_a determined from the Arrhenius dependence includes not only the true activation energy for the reaction of solvent-separated ion-pairs E_s but also a negative quantity ΔH_1 representing the equilibrium between ion-pairs: $E_a = E_s + \Delta H_1(1 - K_1)^{-1}$. The contribution by contact ion-pairs is insignificant, since their reactivity is only 0.1–0.01% of that of solvent-separated ion-pairs, and can be neglected[83]. The activation energy E_a can be either positive or negative depending on the absolute values of E_s and ΔH_1, as well as the value of K_1 at the given temperature.

If the solvent is unable to separate the ion-pairs, the Arrhenius graph will be linear[83,43,95]. The measured k_{ip} constants then represent the reactivity only of contact ion-pairs. For the polymerisation of styrene in dioxan k_{ip} increases[139] in the sequence

$$Li^+ < Na^+ < K^+ < Rb^+ < Cs^+,$$

since increase in the size of the alkali-metal cation facilitates separation of the ionic fragments in the transition state; in this case $\lg k_{ip}$ is a linear function of $(r_{M^+} + 2)^{-1}$, where r_{M^+} is the radius of the cation. On polymerisation of the same monomer in cyclohexane and benzene, in which ion-pairs are definitely of the contact type[65,67], or of α-methylstyrene in dioxan[91], no definite tendency for k_{ip} to vary with the cationic radius is observed, which suggests that other factors are operating, besides the energy of electrostatic interaction between carbanion and gegenion.

It is noteworthy that the characteristics of the solvent—its dielectric constant and solvating power—do not in fact affect the reactivity of contact ion-pairs (Table 11). Rubidium and caesium ion-pairs react at almost the same rate in the polymerisation of styrene in cyclohexane, benzene, dioxan, oxan, and oxolan. Only with the sodium and lithium salts does k_{ip} increase in the sequence dioxan < oxan < oxolan, but this is now due to the participation of solvent-separated ion-pairs in the reaction. It may therefore be assumed that chain growth, like many other bimolecular reactions, involves formation of an intermediate complex, whose conversion into the product is the limiting stage. A similar complex is probably formed also in the reaction between the alkene and the free carbanion. In any case, k_{ion} also does not depend explicitly on the nature of the solvent[96]: in hexamethylphosphoramide, dimethoxyethane, oxolan, oxan, 2-methyloxolan, mixtures of oxolan with dioxan and with benzene, and oxepan it has the respective values 92 000,[42] 40 000,[83] 65 000,[50] 130 000,[140] 30 000,[97] 60 000,[98] 40 000–70 000,[99] and 100 000 [100] $\mathrm{M^{-1}\,s^{-1}}$. We can compare, for example, hexamethylphosphoramide and oxepan: in these solvents the polystyryl anion has almost the same reactivity (k_{ion} = 92 000 [42] and 100 000 [100] $\mathrm{M^{-1}\,s^{-1}}$), although the dielectric constants—30 [110] and 5.06 [100]—differ sixfold. Solvation of the carbanion would obviously play an insignificant part, although it has been adduced[89,90] to explain the effect of an electric field on the rate of the anionic polymerisation of substituted styrenes.

Studies have appeared recently[68,69,136] on the anionic polymerisation of vinyl monomers in the presence of cations of bivalent metals, but analysis of the kinetic data is made difficult by the formation of association complexes and the two-stage mechanism of the dissociation of alkaline-earth metal salts.

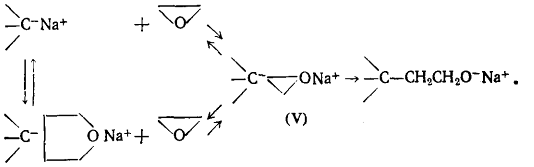
The polymerisation of 2-vinylquinoline[101] and of 2-, 3-, and 4-vinylpyridines[102,135] yields polymers capable of solvating the alkali-metal cation of an ion-pair to a greater extent than the monomers. Furthermore, the nitrogen atom of the pyridyl group is involved in delocalisation of the negative charge[135]: i.e. the growing anion is ambident. The combination of these effects leads to rules characterising the reactivity and the electrical conductivity of alkali-metal salts of these "living" polymers that differ from those observed for such salts of the polystyryl anion.

Table 12. Kinetic parameters[82] of the reactions of sodium salts of 9-substituted fluorenes (9-$\mathrm{RFl^-Na^+}$) with acrylic esters in t-butyl alcohol at 30° C.

Methyl ester	R	10^3k_{ip}, $\mathrm{M^{-1}\,s^{-1}}$	10^3k_{ion}, $\mathrm{M^{-1}\,s^{-1}}$	$\frac{k_{\mathrm{ion}}}{k_{\mathrm{ip}}}$
Acrylate	CN	760	760	1
Acrylate	COOMe	1700	1700	1
Acrylate	$\mathrm{SO_2Ph}$	1600	1600	1
Methacrylate	CN	8.6	8.6	1
Methacrylate	COOMe	10	400	40
Methacrylate	$\mathrm{SO_2Ph}$	34	2200	65
Crotonate	CN	5.2	5.2	1
Crotonate	COOMe	7.6	70	9
Crotonate	$\mathrm{SO_2Ph}$	6.7	690	103

Whereas free carbanions are far more active than contact ion-pairs in the polymerisation of vinyl monomers, these species have in most cases the same reactivity in the reactions of the sodium salts of 9-substituted fluorenes (9-$\mathrm{RFl^-Na^+}$) with methyl acrylate, methacrylate, and protonate in t-butyl alcohol[82] (Table 12). Formation of the Michael product is assumed to have a mechanism of type (15). The variation of the reactivity of the acrylic esters is due both to polar factors and to steric factors (e.g. resulting from introduction of a methyl group).

The formation of intermediate complexes of carbanions and their ion-pairs with electrophiles, leading to a mechanism of type (15), is assumed in nucleophilic substitutions[82], in nucleophilic additions[52,137,138], and in electron-transfer processes[82]. However, it is by no means always possible to detect them: usually only kinetic evidence is available. Such a complex can be detected spectroscopically in the reaction of sodium 9-methylfluoren-9-ide with oxiran[137] in oxan and oxolan at −30° C. The intermediate complex (V) is actually formed by separation of a contact ion-pair by a reactant molecule or by displacement of a solvent molecule from a solvent-separated ion-pair:



(18)

The presence in the epoxide molecule of two centres—electrophilic (a carbon atom) and nucleophilic (the oxygen atom)—makes a push–pull mechanism possible in this reaction[52,137,138], which may be so efficient that the reactivity of the contact type of ion-pair will exceed considerably that of the free carbanion[52,138]. Such is the situation e.g. in the cleavage of the epoxide ring of fluoradenylsodium in oxiran solution[138]. The observed rate constant increases with the concentration of the salt and with the introduction of excess of sodium tetraphenylborate. On the other hand, on the addition of solvating additives—crown polyethers and cryptate (diazahexaoxobicyclic polyether $[\mathrm{N(CH_2CH_2[OCH_2CH_2]_2)_3N}]$)—the rate constant drops sharply. Reaction of the lithium salt of fluoradene is characterised by similar rules. However, the caesium salt is extremely unreactive, perhaps because the large caesium cation is only slightly electrophilic.

Table 13. Kinetic parameters[52] of the reactions of alkali-metal salts of carbanions with oxiran in oxolan at 25° C.

Anion	Cation	k_{ip}, $\mathrm{M^{-1}\,s^{-1}}$	k_{ion}, $\mathrm{M^{-1}\,s^{-1}}$	$\frac{k_{\mathrm{ion}}}{k_{\mathrm{ip}}}$
Polytolanyl	$\mathrm{Na^+}$	0.065	1.1	17
Polystyryl	$\mathrm{Li^+}$	$7.2\cdot10^3$	~200	0,03
Polystyryl	$\mathrm{Na^+}$	13,8		13
Polystyryl	$\mathrm{K^+}$	6.0		33
Polystyryl	$\mathrm{Rb^+}$	3.4		57
Polystyryl	$\mathrm{Cs^+}$	1.7		122
Poly-α-methylstyryl	$\mathrm{Na^+}$	120	2900	24

The importance of the size of the alkali-metal cation for a push–pull mechanism of ring cleavage in oxiran follows also from the data[52] in Table 13. Although the increase in k_{ip} with decrease in cationic size from caesium to sodium in the salts of the polystyryl anion might indicate formally an increase in the contribution by solvent-separated ion-pairs, the sharp drop in k_{ip} on passing to the lithium salt ($k_{\mathrm{ion}}/k_{\mathrm{ip}} \approx 0.3$) can result only from electrophilic collaboration of the lithium cation. The difference in relative reactivities of the carbanions on reaction with the epoxide and with the alkene also suggests that the cation plays an important part in the transition state: in the former case $k_{\mathrm{ion}}/k_{\mathrm{ip}}$ varies between 10 and 100 (Table 13), but in the latter between 1000 and 10 000 (Table 11).

The reactivities of the polystyryl, polytolanyl, and poly-α-methylstyryl anions towards oxiran may be measured by the dissociation constants of their sodium salts[52]: k_{ion} is greater the smaller is K_{D}, and the dependence of lgk_{ion} on lgK_D' is linear. Thus the dissociation constant reflects the stability of these species, as in the case of the anions of 9-substituted fluorenes.

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The Structural Factors and Reactivity of Biphenyl

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Data on the structure, conformations, and reactivity of biphenyl in solutions have been examined critically and the importance of the conformational factor for the reactivity of biphenyl is repudiated.
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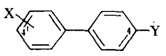
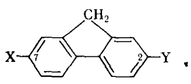
I. INTRODUCTION

The electrophilic substitution and displacement reactions involving a substituent in the 4-position in biphenyl have been widely investigated. A careful study by Stock and Brown[1] has shown that in reactions of this kind biphenyl does not obey the Selectivity Relations for the SE reactions of a series of monosubstituted benzenes. The behaviour of biphenylylene systems (I) in transmitting the electronic influences of substituents to the reaction centre in the 4-position is also unusual. Their capacity for transmitting such effects is greatly reduced compared with the corresponding phenylene and certain bridged structures, where the aromatic rings are separated by an atom with a lone electron pair[2,3]:



(I)



(II)

The cause of most of these specific phenomena has been recognised[1,2] as the non-coplanarity of the aromatic rings of biphenyl in solution, which may appreciably disrupt the conjugation between them. The possibility of the system becoming coplanar in the transition state has been regarded as significant[1,2]. In particular, a confirmation of this hypothesis has been seen in the greater reactivity of the 2-position of the planar fluorene molecule (II, X = Y = H) when account is taken of the possible influence of the methylene units and also, seemingly, in the fact that fluorene obeys satisfactorily the Selectivity Relations for a series of monosubstituted benzenes[1]. On the other hand, the possibility of different degrees of conjugation between the non-attacked ring and the reaction centre as a function of a measure of the electrophilic properties of the reactant has been postulated for biphenyl[4-6]. The conformational factor was not regarded as of decisive importance[5,6], but the evidence for this was probably insufficient[1,6].

II. CONFORMATIONAL ANALYSIS OF BIPHENYL

Numerous studies have been devoted to the problem of the steric structure of biphenyl. In the crystalline state the benzene rings are located in the same plane[7-15]. The rings in the biphenyl molecule in the vapour state are not in the same plane and the dihedral angle between their planes is 42–45°.[16-19] The non-planar conformation of the isolated molecule has been explained theoretically as a consequence of the repulsion of atoms not linked by valence forces[20-31].

Direct X-ray and electron diffraction methods, which are effective in the determination of the conformations in the crystalline and vapour states of biphenyl, are unsuitable for its solutions. The results obtained by other methods are contradictory, but the reasons for this have not been discussed. The appreciably lower degree of displacement from coplanarity or even the absence of coplanarity for the molecule in solution compared with the vapour state can be readily accounted for. The low energy barrier to the rotation of the biphenyl rings from the equilibrium to the planar disposition, which amounts to 0.4–4.0 kcal $mole^{-1}$ according to various estimates[21-23,26,27,29,31-34], is evidently overcome when the molecules are packed to form crystals. Since the effective volume of the molecule with the coplanar disposition of the rings is smaller than for the non-coplanar disposition, the internal pressure factor of the solvent should promote the former[35]. The dependence of the conformation of biphenyl, determined from vibrational spectra, on the nature of the solvent has been stressed[36]. The planar conformation of the solute molecule predominates in a structured solvent forming hydrogen bonds, probably owing to the ordering of the species in the environment or owing to unexplained specific effects. Thus the nature of the medium may be responsible for the ambiguity of the results of conformational analysis.

In the number of studies dealing with the vibrational spectra of biphenyl in solutions and in the melt, a qualitative conclusion was reached that the molecules are to some extent non-coplanar[37-42]. The angle of twist of the molecule has been estimated as 22–45° from the shift or changes in the intensities of the vibrational bands when crystalline biphenyl melts or is dissolved[43-48]. On the other hand, the vibrational spectra of biphenyl or its deutero-analogues in solution or in the melt have been interpreted[32,49-52] on the assumption that the conformation is planar.

According to ultraviolet spectroscopic data, biphenyl has an intense (ϵ = 17 000–19 000) conjugation band near 250 nm, corresponding to the first $\pi-\pi^*$ electronic transition, which has been attributed both to the planar conformation[53-55] and to the fact that the angle between the fragments is appreciably less than 45° ($\leqslant$ 20°).[56-63] Measurements of the anisotropy of the electrical polarisability[64] and diagmagnetic susceptibility[65] have led to the conclusion that the rings of the biphenyl molecule are located in the same plane in solutions.

The conformation of biphenyl in solution has been investigated in relation to biphenyl itself and its derivatives also using dipole moment[66] and light scattering[67–69] methods, electron paramagnetic resonance of the radical-anions[70,71], and NMR in the nematic phase[72]. Semi-empirical quantum-chemical calculations have been made of the conformation of biphenyl from its reactivity in nitration[73]. In some of these studies the dihedral angle between the planes of the rings was estimated as less than or equal to 30°,[66,68,69,71,72] while in others the closeness of the rings to the coplanar disposition was pointed out[67,70,73].

Thus theoretical and experimental studies (about 50 in all) on the conformations of biphenyl in solutions do not provide an unambiguous solution to the problem. However, as mentioned above, it has usually come to be assumed that biphenylylene systems and biphenyl itself are non-coplanar in solutions, like biphenyl in the gas phase, and the nature of their reactivities has been determined on this basis[1,2]. As will be shown below, this approach is unjustified, at least in relation to biphenyl.

III. STRUCTURAL FACTORS AND CONJUGATION IN BIPHENYL

Despite the fact that the ambiguity of the results of the determination of the conformation of biphenyl in solutions may be to some extent attributed to the very nature of the phenomenon (see, for example, Wilk[36]) a definite trend concerning the methods of investigation may be observed in the complete set of the available literature data. A planar or nearly planar conformation of biphenyl is indicated by methods involving the measurement of physical parameters about the direct dependence of which on conjugation (in this instance between the phenyl fragments) there is no doubt: the position and intensity of the long-wavelength absorption band in the ultraviolet spectrum[59a, 56], the anisotropy of the electrical polarisability of the molecules (the Kerr electro-optical effect[64]), and their diamagnetic susceptibility (the Cotton–Mouton effect[65]).

In biphenyl, which constitutes a weakly conjugated system comprising two aromatic rings[41,74], the conjugation depends on the angle between the planes of the rings and on the length of the central bond. As regards the relation between these two factors, until recently in theoretical studies the length of the bond between the rings was assumed to be constant for different angles of rotation or it was assumed that, as the angle between the planes of the rings increases, the degree of conjugation falls and there is a corresponding increase in the length of the bond[25,62,73,75]. However, experimental data indicate the opposite: as the biphenyl molecule ceases to be planar, i.e. when biphenyl passes from the crystalline to the vapour state, the length of the bond between the rings diminishes[12,13,17–19] approximately by 0.008–0.018 Å owing to the rapid decrease of the repulsive force between non-bonded atoms. This fact began to be taken into account very recently in quantum-chemical calculations on the biphenyl molecule[27,29,30], which is quite justified because the usual accuracy in the determination of the length of bonds between carbon atoms is to within 0.002 Å.[76]

So yet another cause of the contradictory results of the determination of the angle of twist of the central bond of biphenyl in solution become understandable. Methods where the degree of conjugation between the fragments is determined do not indicate or scarcely indicate the differences between the planar molecule (crystalline state) and the molecule in solution; there might be no difference, if, firstly, the conjugation were virtually independent of the type of conformation or, secondly, if under these and other conditions the molecule were planar. The second possibility must be rejected in the general case according to the results of studies by other methods. Thus careful analysis of the symmetry of the molecule on the basis of infrared and Raman spectra of biphenyl in the melt and in solutions, i.e. by methods which are not related to the conjugation between the rings, reveal a D_2 symmetry group or a non-polar conformation[39]; the same conclusion was reached by the authors of a number of other studies mentioned above. However, the first possibility remains.

Calculations have shown that the conjugation of the rings in biphenyl can indeed be independent of the angles between their planes when the latter are small (this is probable and is characteristic of biphenyl in solution). The ring conjugation energy found by different workers is 5–7 kcal mole^{-1}.[74] It is usually believed that this quantity is equal to the increase of the energy of the central bond owing to its π-component compared with the energy of a single bond between trigonal carbon atoms. When the rings rotate by an angle φ = 30–45°, the conjugation energy decreases in proportion to $\cos^2\varphi$,[77] i.e. by 1.5–3.0 kcal mole^{-1}. However, this would be true for a constant length of the central bond, whereas in reality the latter diminishes. The energy increment owing to the contraction of the bond may be estimated, for example, by employing the proportionality between the order and length of the bond, on the one hand, and between its order and its energy, on the other[78a,79]. More correct values should be obtained using Dewar and Schmeising's tractrix equation[80] for the relation between the length and energy of a bond of this kind. Similar ranges of values correspond to both methods of calculation: 1.8–3.9 and 1.5–3.4 kcal mole^{-1} respectively. In order to determine the increase in the energy of the π-component, it is necessary to introduce a correction for the change in the σ-component, which is positive or negative depending on what value is adopted for the equilibrium length of a "single" C_{sp^2}–C_{sp^2} bond—greater or smaller than in biphenyl. However, there is at present no definite answer to the question of the length of this bond: investigators have expressed divergent views and the range of probable values is 1.48 to 1.53 Å.[27,28,59c,78b,81b] Nevertheless, if the correction to the change in the σ-component for different probable lengths of the σ-bond is calculated using the harmonic approximation to the Morse curve[82a], values not exceeding 0.3–0.6 kcal mole^{-1} are obtained; in our discussion they can be disregarded. A stabilisation energy of the π-component of the bond between the rings similar to the values obtained above, which is up to 3.0 kcal mole^{-1} and depends on the contraction of the bond, can be derived from the dependence of the "spectroscopic" resonance integral on the distance between the carbon atoms[59c].

We thus see that the decrease of the conjugation energy owing to the rotation of the biphenyl rings may be compensated by the simultaneous contraction of the bond between the rings, particularly if account is taken of the fact that the angle of rotation may be much less than 30 to 45° and a significant contraction of the bonds between the biphenyl ring should occur even when their angles of rotation are small, owing to the rapid weakening of the nonbonding interactions in systems of this kind[27,59d].

The changes in the energy of the π-component of the bond can be set equal to the changes in the π-electron energy of the molecule[82b] and, if the latter are small or absent, then, for methods where the degree of conjugation is measured, the difference between the planar and slightly staggered molecular systems vanishes. One must therefore agree with the claim that the "estimation of the twist angles from ultraviolet spectra in such systems is extremely doubtful and risky, since... spectra calculated from the results of conformational analysis are almost independent of the twist angle"[83]. The phenomenon under discussion can thus be regarded as experimentally and theoretically well-founded.

This claim may not prove to be entirely correct, since in a number of studies[56-63] based on ultraviolet spectroscopic data small but significantly non-zero twist angles have been obtained for the central bond of biphenyl in solution, namely 18–23°. However, when the position of the first ultraviolet band of biphenyl in the spectra of solutions is compared with that in the spectra of the crystalline material, a correction must be applied for the "red shift" in the spectrum of the crystals. Its actual value for biphenyl is unknown and the arbitrary nature of the selection of such corrections[59e] virtually permits the assumption that the difference between the band positions is zero. If a small difference (1.5–3 nm or of 0.7–1.4 kcal mole^{-1}) between the energies of the $\pi-\pi^*$ transitions in both states remains even after the introduction of the correction, it may be caused by the distortion of the molecular skeleton of biphenyl in the crystal field[12-15], which should lead to a bathochromic shift of the conjugation band[59,84,85].

The extinction coefficient of the $\pi-\pi^*$ transition band in the biphenyl crystal cannot be determined owing to technical difficulties[57]. On the other hand, in the estimation of the angle of twist of the bond between the rings by comparing the extinction coefficients of this band in solutions of biphenyl and planar fluorene, the entire difference between them was attributed[56] solely to the non-coplanarity of the rings of the former. However, in the fluorene molecule the central bond is shorter than in biphenyl. This follows both from experimental data[86] and from a comparison of the results of semiempirical quantum-chemical calculations using the σ^+_{Ar} constants for the above compounds[87]. The greater intensity of the fluorene band may be caused in addition by the specific influence of the bridge group[88]. It is therefore of interest to note that biphenyl in solution exhibits a somewhat more intense conjugation band than 9,10-dihydrophenanthrene (φ = 20° according to the model)[89].

Quantitative allowance for the above correction factors is extremely difficult or impossible. However, without it the instances of the application of ultraviolet spectroscopic methods to the conformational analysis of biphenyl can be used merely for the purpose of illustration.

The problem of the role of the conjugation between the rings in the study of the vibrational spectra of biphenyl is probably less well defined in view of the complexity of the interactions between the electronic and vibrational levels. The role of such conjugation varies as a function of the choice of particular bands and presumably the validity of the band assignment does not always guarantee the reliability of the final conclusions, because it is also not clear to what extent the crystalline state of the molecule may serve as an adequate model for the planar conformation. It is therefore difficult to give preference to the results of one study rather than another. Qualitative conclusions about the type of conformation based on the analysis of the symmetry of the molecule in solution are for this reason most significant.

IV. THE STRUCTURE AND REACTIVITY OF BIPHENYL IN SOLUTIONS

The foregoing considerations throw serious doubt on the validity of many postulates which have come to be widely held, namely:

(1) the low transmission coefficient of the *p*-biphenylylene system $\pi' = \rho_{\text{p-C}_6\text{H}_4\text{C}_6\text{H}_4}/\rho_{\text{p-C}_6\text{H}_4} \simeq 0.3$ can be accounted for by its non-coplanarity[2];

(2) the failure of biphenyl to obey the Selectivity Relations for the series of monosubstituted benzenes can be accounted for by the non-coplanary of its molecule[1];

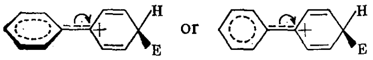
(3) the behaviour of fluorene as regards Selectivity Relations is different to that of biphenyl (a claim which aroused controversy at one time)[1,6,90];

(4) when account is taken of the activating influence of the bridge unit, the reactivity of fluorene in electrophilic substitution in the 2-position exceeds that of biphenyl in the 4-position owing to the non-coplanarity of the molecule of the latter[1].

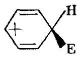
Bearing in mind the considerations set out in the previous section, we shall examine these postulates in greater detail.

1. The low transmission coefficient π' of the biphenylylene molecular system (I) cannot be explained by its non-coplanarity, because the values of π' for the analogous fluorenylene system (II) are significantly the same[3,91]. We were unable to find any literature data on which a different claim could be based and were forced to conclude that the opposite views[2] are in all probability due to a misunderstanding.

2. The reactivity of biphenyl is higher than that of benzene owing to ring conjugation[92], which facilitates electron transfer to the reaction centre [ions (III) and (IV), *E* being an electrophile].

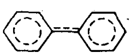


(III)



(IV)

The conjugation effects are most important in highly selective reactions with large values of the constant ρ^+; according to modern views, the transition states in such reactions are structures closest to those of carbonium ion σ-complexes. For the most selective of the known reactions—molecular bromination ($\rho^+ = -12.1$)—the 4-position in biphenyl is more reactive than a single position in the benzene ring by a factor of 2920.[1] This is equivalent to a difference between the free energies of activation amounting to $\Delta\Delta F^{\neq} = (RT \lg 2920)/\lg e \simeq 5$ kcal mole^{-1}, which corresponds to the energy of conjugation via the central bond. The agreement in this instance is probably not fortuitous and this approach reveals an interesting aspect of the comparison of kinetic and thermodynamic (structural) factors in reactivity. The characteristic feature of the molecular structure of biphenyl (I′)



(I′)

namely that the bond between the rings (as well as the atoms involved in it) contributes a definite additional $\pi(p)$-electron density, is manifested by the corresponding stabilisation of the transition state, which is evident from a comparison of ions (III) and (IV). In this approach there is no justification for postulating the inclusion of rotation and mutual approach of the rings in the reaction coordinate[1]. Evidently the conformational factor is immediately excluded from consideration if the initial state in solution involves a predominately planar conformation. The opposite case must in fact be considered.

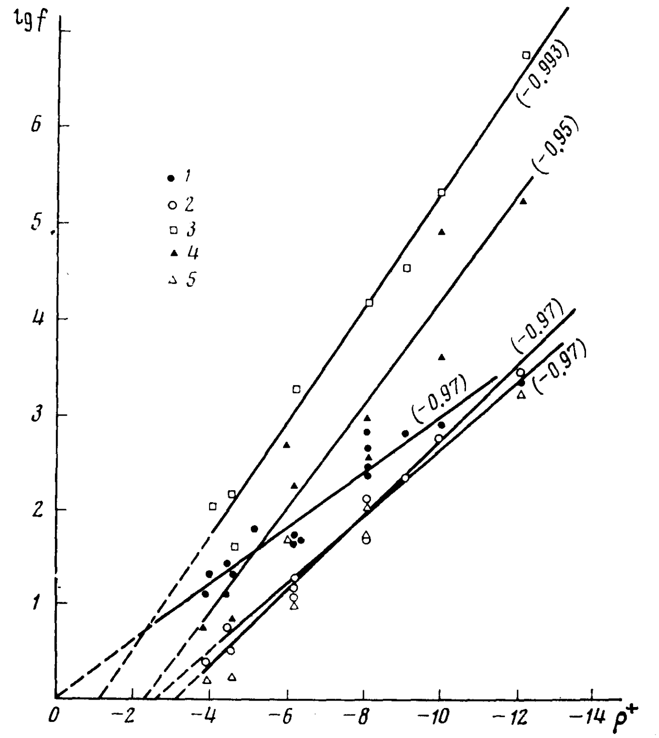
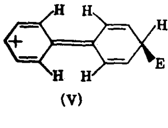


Figure 1. Dependence of the logarithms of the partial rate factors on ρ^+ in reactions with moderate and high selectivities[1] (the correlation coefficients are indicated in brackets): 1) *p*-tolyl; 2) 4-biphenylyl; 3) 2-fluorenyl; 4) 1-naphthyl; 5) 2-naphthyl.

Biphenyl does not obey Selectivity Relations for monosubstituted benzenes, which is evident from a comparison with toluene in Fig. 1. In reactions with moderate and high selectivities involving biphenyl the linear plot of $\lg f_{4\text{-Ph}}$ against ρ^+ (f is a partial rate factor) does not pass through the coordinate origin and has a higher slope than the analogous plot for toluene. In the most selective reaction (molecular bromination), the *para*-position in biphenyl is actually more reactive than in toluene. The explanation of these phenomena, involving the hypothetical carbonium ion (V)



(V)

as the model of the transition state, appears to be unlikely, as well as the claim that the degree of stabilisation of such an ion increases as a result of the contraction of the bond between the rings[1]. Indeed comparison of ion (V) not only with ion (III) but also with ion (IV) reveals that the formation of its structure requires an additional energy expenditure in order to disrupt the second aromatic π-electron sextet, to overcome the barrier to rotation, and to overcome increased non-bonded repulsions—in all about 60 kcal mole^{-1} (36 + 4 + 20 kcal mole^{-1} respectively; the non-bonding repulsion was estimated from known potential functions[28]). It is difficult to specify an energy source whereby such expenditure could be compensated. On the other hand, it is evident that a definite energy gain corresponds to structure (III).

The lower reactivity of biphenyl compared with toluene in the majority of reactions (Fig. 1) likewise need not be explained by the presence of an energy barrier to the rotation of the rings[1]. Using modern ideas about the transition state in electrophilic aromatic substitution as the product of the overall contribution of the σ- and π-complex structures[93,94], it is easy to find an acceptable explanation. For ionic or highly polar reactants (low values of ρ^+), the structure of the transition state is closer to that of π-complexes and the negative inductive effect of the phenyl substituent as well as the positive inductive effect of the methyl group begin to play an important role.

Thus, consideration of the reactivity of biphenyl does not require its molecular system to be coplanar in the transition state. Here it is important to know a significant fact—the equality of the entropies of activation for biphenyl, fluorene, and 9,10-dihydrophenanthrene in one of the most selective reactions—molecular chlorination[95]. Since biphenyl should possess some freedom of rotation of the rings about the central bond in solution (initial state), this finding does not support model (V) for the transition state.

The nature of the reactivity of biphenyl suggests that it can be only formally included among monosubstituted benzenes and that in essence it gravitates towards the group of polycyclic hydrocarbons (Figs. 1 and 2). Their distinctive features are a large size and conjugation of the π-electron systems. In general this creates better conditions for the delocalisation of the positive charge in the substitution step than in the usual benzene derivatives. The observed rates of highly selective reactions for compounds of this kind are much higher than would follow from the Selectivity Relations for monosubstituted benzenes. The foregoing is illustrated in Fig. 2 for the molecular chlorination and bromination reactions. A similar phenomenon has also been observed for the sulphonation of nitrobenzene with sulphuric acid ($\rho^+ = -10$).[99] Evidently the behaviour of biphenyl shows a greater similarity to that of fluorene, naphthalene, and other polycyclic hydrocarbons than to monosubstituted benzenes. It is striking that the reactivities of the 1- and 2-positions in naphthalene in relation to moderately selective reagents are several times lower than that of the *para*-position of toluene, whereas in the highly selective chlorination and bromination reactions naphthalene is more reactive than toluene by several orders of magnitude[1]. This finding can be explained, so far only qualitatively, on the basis of the same hypotheses as in the case of biphenyl.

3. One of the main pieces of evidence quoted by Stock and Brown[1] against Neuman's objection[6] to their conclusion that biphenyl and fluorene behave differently in electrophilic substitution is the, at first sight, greater variation of the $\sigma^+_{4\text{-Ph}}$ constants in various reactions compared

with the $\sigma^+_{2\text{-Fl}}$ constants. However, the present author believes that in this case one can only speak of the variation of free energies, i.e. of the absolute and not relative variations of the constants. Fig. 3 clearly shows that the variation of the free energy of activation in the reactions of fluorene on average exceeds the corresponding variation for biphenyl. The problem of the causes of such variation is not the subject of the present review[99,100]. We shall also set aside the problem of the existence of a single scale of the Hammett–Brown constants for polycyclic hydrocarbons, applicable to all electrophilic substitution reactions. In view of the specific nature of polycyclic hydrocarbon systems, they cannot be accommodated within the same framework with monosubstituted benzenes. This fact is very likely to underlie the phenomenon under consideration.

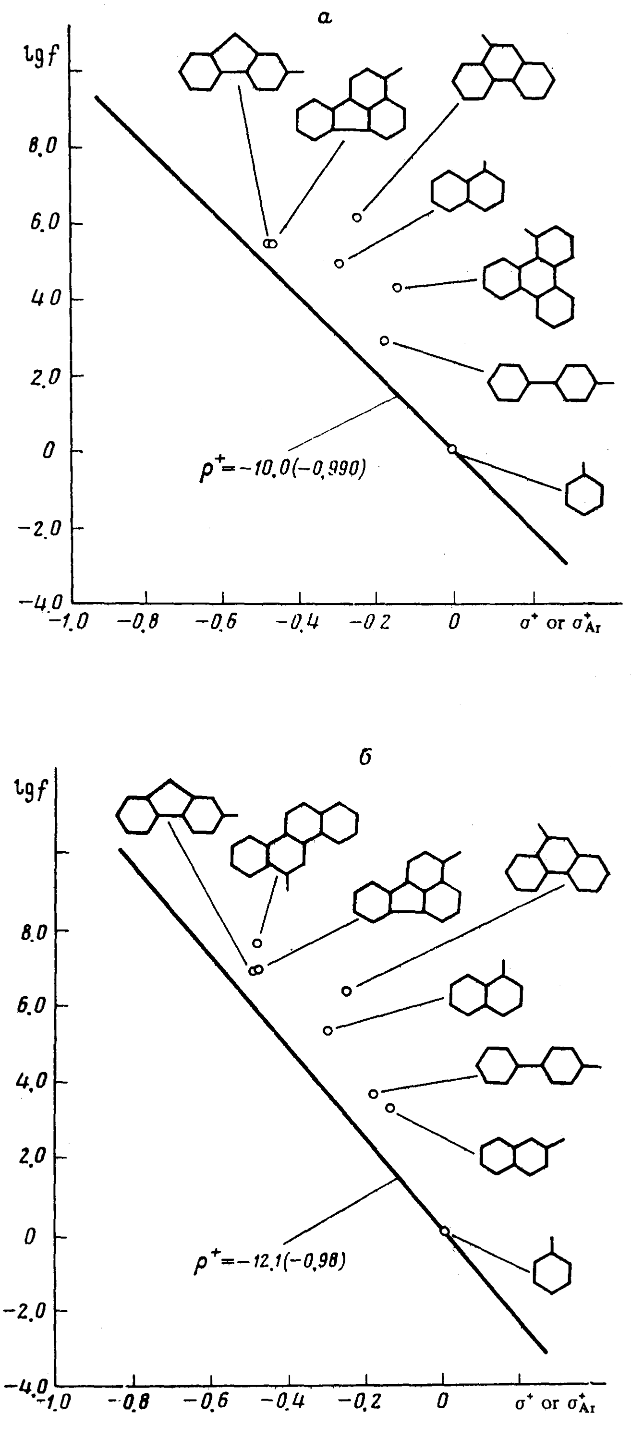


Figure 2. The Selectivity Relation for monosubstituted benzenes (straight lines) and for polycyclic hydrocarbons (circles): *a*) molecular chlorination in acetic acid[1,81b]; *b*) molecular bromination in acetic acid[1,96]. The values of σ^+_{Ar} were taken from Refs. 97–99 or calculated by Kachurin's method[99] from data quoted by Streitwieser[81c]; the correlation coefficients for monosubstituted benzenes are indicated in brackets.

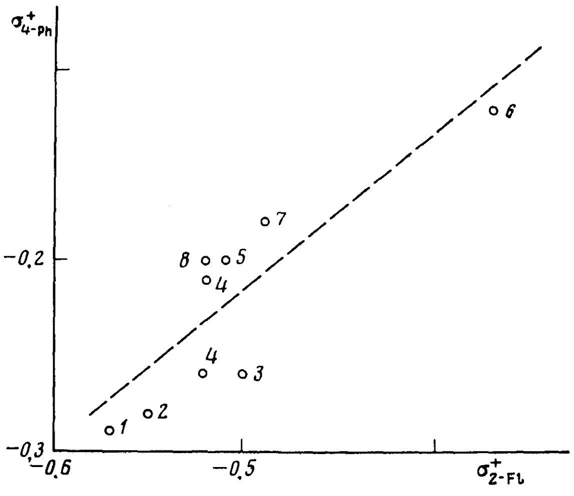


Figure 3. Variation of the constants $\sigma^+_{4\text{-Ph}}$ and $\sigma^+_{2\text{-Fl}}$ in various reactions[1] (the constants ρ^+ are indicated in brackets): 1) bromination (–12.1); 2) chlorination (–10.0); 3) acetylation (–9.1); 4) protodetritiation (–8.1); 5) nitration (–6.2); 6) protodesilylation (–4.6); 7) solvolysis of t-cumenyl chlorides (–4.5); 8) mercuration (–4.0); the slope of the dashed straight line is 0.83.

4. There is no need to resort to the conformational factor also in the treatment of the differences between the reactivities of fluorene and biphenyl. Compared with biphenyl, the bond between the rings in fluorene is shorter by 0.011–0.021 Å.[12,13,86] Using the average value 0.016 Å we find (see Section III) that it corresponds to an additional conjugation energy of 2.5 kcal mole^{-1} or to an acceleration of the highly selective reaction by a factor of ~ 70. If account is taken of the influence of the methylene bridge group[1], good agreement with experiment is achieved. This result is particularly interesting in view of the fact that quantum-chemical methods did not yield an interpretation of the reactivity of fluorene consistent with experiment and it was necessary to resort to the strained ring hypothesis[101-103].

Thus the characteristic behaviour of biphenyl in electrophilic substitution reactions can hardly be legitimately explained by the non-coplanarity of its molecule in solution.

Biphenyl is a special case of a substrate whose structure is intermediate between that of monosubstituted benzenes and polycyclic hydrocarbons. In contrast to the latter, the bond between the aromatic fragments of its molecule is appreciably weakened. The central bond is sometimes actually regarded as in essence a single bond[78c]. This fact is important for the understanding of the set of data known as the positive bridge effect, the conditions for the manifestation of which have been examined in a recent review[3].

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γ-Piperidinones in Organic Synthesis

N.S.Prostakov and L.A.Gaivoronskaya

Methods for the synthesis of γ-piperidinones and their derivatives, including physiologically active compounds, are considered and the results of studies designed to establish the structures of certain tertiary γ-piperidinols are discussed. Research on the applications of γ-piperidinones in the syntheses of various heterocyclic compounds is surveyed.
The bibliography includes 415 references.

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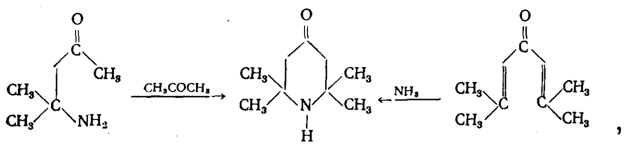
I. INTRODUCTION

Among piperidine derivatives, γ-piperidinones are of primary importance from synthetic, theoretical, and applied standpoints. The development of the synthetic chemistry of piperidine and of the conformational analysis of substituted piperidine bases as well as the synthesis of effective medicinal drugs and of new nitrogen-containing heterocyclic systems are all branches of the chemistry of heterocyclic compounds associated with γ-piperidinones.

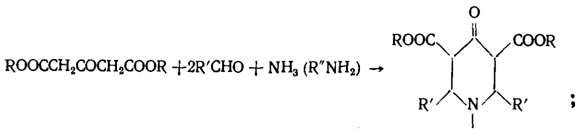
This paper deals with studies carried out mainly in the last twelve years, which characterise the development of certain branches of the chemistry of piperidine and of heterocyclic compounds related synthetically to γ-piperidinones. Studies designed to determine the steric structures of tertiary γ-piperidinols—the starting materials for the synthesis of effective analgesics—are also considered. In the solution of the problems of the configuration and conformation of compounds of this type contradictory conclusions have sometimes been reached. Numerous experimental data have now been obtained, which makes possible an objective and correct conclusion about the steric structures of γ-piperidinols.

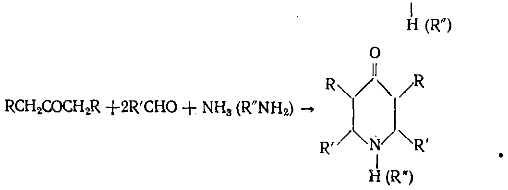
The methods of synthesis of γ-piperidinones are comparatively limited, and can be assigned to two groups as regards the type of reactions involved.

1. The condensation of carbonyl compounds with ammonia or primary amines: of acetone with ammonia (the synthesis of triacetoneamine), of diacetoneamine with ketones, of acetonedicarboxylate esters with aldehydes and ammonia or primary amines, of ketones of β-ketoacid esters with aldehydes and ammonia or primary amines, and of divinyl ketones with ammonia or primary amines. The methods of synthesis of γ-piperidinones from 2-cinnamoyloxirans and primary amines[1,2], from alkenyl β-diethylaminoethyl ketones and methyl amine[3,4], and from diacetone alcohol, ketones, and ammonia[5] are similar to the last method described above. The first γ-piperidinone—2,2,6,6-tetramethyl-4-piperidinone—has been synthesised by the above procedures:

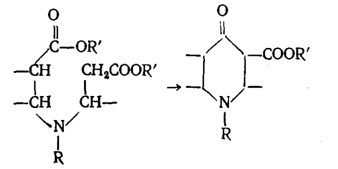


as well as many γ-piperidinones with different ring substituents:





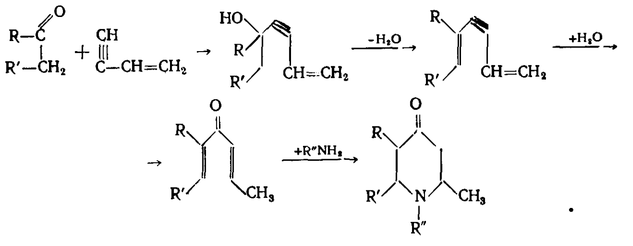
2. Cyclisation of aminodicarboxylate esters by the Dieckmann method:



The bibliography of many studies concerning the development of methods of synthesis of γ-piperidinones has been published by Bel'skii et al.[6]

The alkylation and acylation of γ-piperidinones unsubstituted at the nitrogen atom as well as their cyanoethylation have been described. The synthesis of *N*-halogeno-γ-piperidinones has been reported. Treatment of triacetoneamine with perchloryl fluoride led to the isolation of 1-fluoro-2,2,6,6-tetramethyl-4-piperidinone[7]. When 2,5-dimethyl-4-piperidinone hydrochloride is treated with sodium hypochlorite, 1-chloro-2,5-dimethyl-4-piperidinone is formed and is then converted under alkaline conditions into 2,5-dimethyl-1,2-dehydro-4-piperidinone. The latter was isomerised to 2,5-dimethyl-5,6-dihydro-4-pyridone[8]. 1-Amino-2,6-diphenyl-4-piperidinone has been isolated on reducing the corresponding *N*-nitrosopiperidinone with lithium tetrahydroaluminate[9]. Bis-(2,2,6,6-tetramethyl-4-oxo-1-piperidyl) disulphide, which is formed on treating triacetoneamine with sulphur dichloride, dissociates at temperatures in the range 90–200°C with formation of stable radicals[10]. It has been established by spectroscopic methods that the tautomeric equilibrium involving 3,5-diethoxycarbonyl-4-piperidinones is to a large extent displaced towards the enolic form, which is stabilised as the chelate[11]. The ketonic and enolic forms of 3,5-diethoxycarbonyl-1-ethyl-2,6-diphenyl-4-piperidinone have been isolated[12]. The ratio of the *cis*- and *trans*-isomers of 1-alkyl-2,5-dimethyl-4-piperidinones has been determined chromatographically as a function of different substituents at the nitrogen atom. Under alkaline conditions, the equilibrium is displaced towards the *cis*-form on passing from the methyl to the t-butyl group[13].

Nazarov and his coworkers have made a significant contribution to the development of the chemistry of γ-piperidinones. The consecutive reactions which they devised, namely the condensation of vinylacetylene with ketones and dehydration of the resulting vinylacetylenic alcohols to divinylacetylenic hydrocarbons followed by the hydration of the latter to divinyl ketones, constitute a simple and easy method of synthesis of these previously difficult to obtain compounds.



Before Nazarov's work, the only divinyl ketone derivatives used in the syntheses of γ-piperidinones were phorone and dibenzylideneacetone. Nazarov's method made it feasible to synthesise γ-piperidinones with a wide variety of substituents in the piperidine ring, the mode of substitution depending on the structure of the ketones used in the condensation with vinylacetylene. 1,2,5-Trimethyl-4-piperidinone is synthesised by this method under industrial conditions[14].

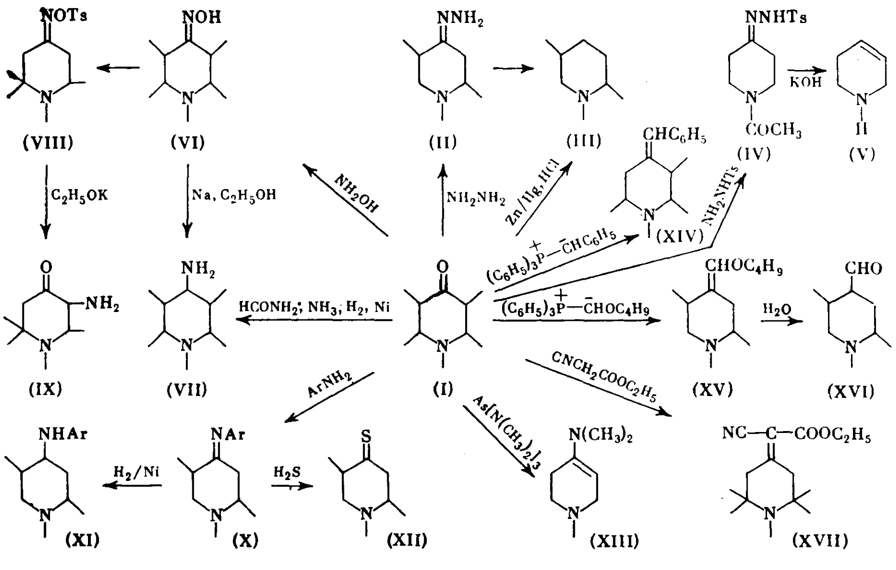
Tetrahydro-γ-pyrones, which are obtained, like γ-piperidinones, from divinyl ketones, are converted into γ-piperidinones by reaction with primary amines[15–17]. The conversion of 2,6-dimethyl-4-pyrone into 1,2,6-trimethyl-4-piperidinone via 1,2,6-trimethyl-4-pyridone and 1,2,6-trimethyl-4-piperidinol has been described[18].

A wide variety of reactions of γ-piperidinones involving the carbonyl group have been examined in a number of studies (Schemes 1 and 2). The reduction of γ-piperidinones (I) to piperidines (III) has been achieved via their hydrazones (II) [9,19–25] and also by the Clemmensen method [25]. Thermal decomposition of 1-acetyl-4-piperidinone toluene-*p*-sulphonylhydrazone in the presence of potassium hydroxide gave a quantitative yield of 1,2,5,6-tetrahydropyridine (V).[26] 1-Acetyl-3-ethoxycarbonyl-4-piperidinone was converted similarly into 1,2,5,6-tetrahydronicotinic acid[27]. The hydrazones of triacetoneamine substituted in the amino-group[28] as well as the hydrazones of this piperidinone with different substituents at the ring nitrogen atom (hydroxy-, nitroso-, etc.)[29] are used as polymer stabilisers. After the oxidation of 3,5-dimethyl-2,6-diphenyl-4-piperidinone semicarbazone with $[2NH_4NO_3\cdot Ce(NO_3)_4]$, a similarly substituted piperidinone was isolated. Its configuration has been determined[30].

The replacement of carbonyl oxygen by an amino-group in γ-piperidinones has been achieved by reducing their oximes (VI),[21,31–33] by the reaction of the piperidinones with formamide[34], and by reductive amination[35,36]. A number of acyl derivatives of γ-aminopiperidinones (VII) obtained in this way have been described[37]. β-Amino-γ-piperidinones (IX) have been synthesised by treating the sulphonate esters of γ-piperidinone oximes (VIII) with potassium ethoxide[38]. A number of Schiff bases (X), obtained from γ-piperidinones and primary amines, have been described; some of them have been reduced to aryl-(4-piperidyl)amines (XI).[39–43] Treatment of *N*-(1,2,5-trimethyl-4-piperidylidene)aniline with hydrogen sulphide yielded 1,2,5-trimethyl-4-thiopiperidinone (XII).[44] The hydrochloride of 1-methyl-4-thiopiperidinone was isolated in the form of a polymer after treating 1-methyl-4-piperidinone with hydrogen sulphide in an alcoholic solution of hydrogen chloride[45].

The interaction of 1-methyl-4-piperidinone with tris-(dimethylamino)arsine led to the formation of an enamine derived from piperidine, namely 1-methyl-4-dimethylamino-1,2,5,6-tetrahydropyridine (XIII).[46] Its analogue, 1-benzyl-5-methyl-4-(1-pyrrolidinyl)-1,2,5,6-tetrahydropyridine, has been described[47]. 4-Benzylidene-2,6-dimethyl- and 4-benzylidene-3-methyl-2,6-diphenylpiperidines (XIV) have been synthesised by the interaction

Scheme 1



of the corresponding piperidinones with triphenylbenzylidenephosphine[48]. (1-Methyl-$\Delta^{4,\alpha}$-4-piperidyl)acetonitrile and ethyl (1-methyl-$\Delta^{4,\alpha}$-4-piperidyl)acetate have been synthesised by the Wittig reaction from 1-methyl-4-piperidinone[49]. An analogue of the ethyl ester with a benzoyl group attached to the nitrogen atom has been described[50]. Ethyl (1-benzoyl-3-ethyl-$\Delta^{4,\alpha}$-4-piperidyl)acetate has been obtained by the same procedure[51]. Hydrolysis of 4-butoxymethylene-1,2,5-trimethylpiperidine (XV), which is obtained from 1,2,5-trimethyl-4-piperidinone and butoxymethylenetriphenylphosphine, results in the formation of 4-formyl-1,2,5-trimethylpiperidine (XVI)[52]. This aldehyde has also been obtained from the same piperidinone and chloromethyl ether[53].

(2,2,6,6-Tetramethyl-4-piperidylidene)cyanoacetate ester (XVII), formed on condensation of the cyanoacetate ester with triacetoneamine, is used as an intermediate in the synthesis of the medicinal drug "Temekhin"[42,54]. An analogous compound has been described[55]. The condensation of 1,2,6-trimethyl-4-piperidinone with malonodinitrile gave 4-dicyanomethylene-1,2,6-trimethylpiperidine[56].

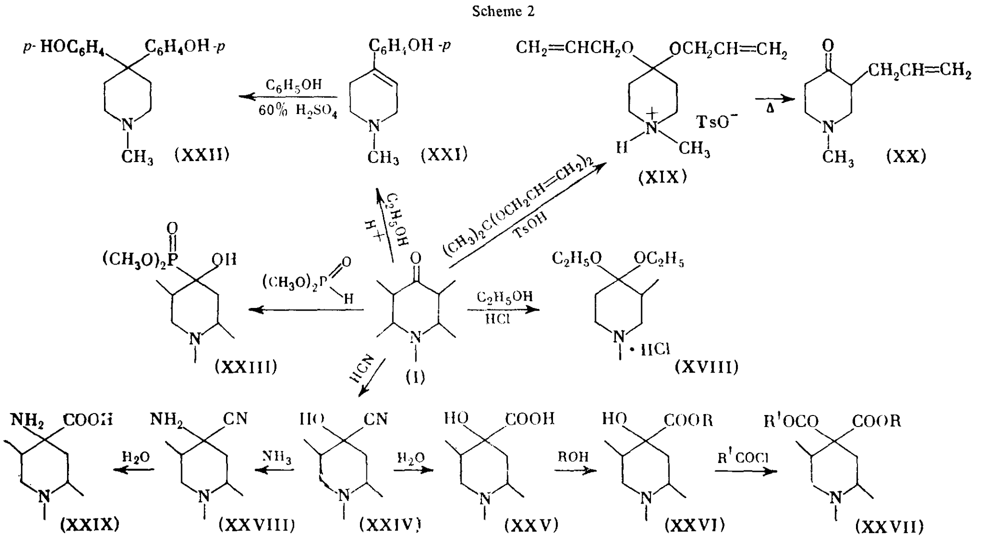
Scheme 2 presents reactions involving addition to the carbonyl group of γ-piperidinones. Triacetonamine ketals have been obtained by treating triacetoneamine with a mixture of the alcohol and benzene in the presence of toluene-*p*-sulphonic acid[57]. On crystallising γ-piperidinone hydrochlorides from an ethanol–ether mixture, their diethyl ketals (XVIII) are readily formed[58,59]. The quaternary salt (XIX) of toluene-*p*-sulphonic acid and 4,4-diallyloxy-1-methylpiperidine, obtained from piperidinone and acetone diallyl ketal in the presence of toluene-*p*-sulphonic acid, was converted into 3-allyl-1-methyl-4-piperidinone (XX) by heat treatment[60]. The condensation of 1-methyl-4-piperidinone with phenols under acid conditions has been investigated. Condensation with phenol led to the isolation of 4-(*p*-hydroxyphenyl)-1-methyl-1,2,5,6-tetrahydropyridine (XXI), which is converted into 4,4-di-(*p*-hydroxyphenyl)-1-methylpiperidine (XXII) on further interaction with phenol[61].

The condensation of 2,5-dimethyl- and 1,2,5-trimethyl-4-piperidinones with dimethyl phosphite has been achieved which led to the formation of 2,5-dimethyl and 1,2,5-trimethyl-4-(OO-dimethylphosphono)-4-piperidinols (XXIII)[62,63]. Diallyl phosphite and dipropargyl phosphite were used in analogous syntheses[64]. The usual procedures have been used to synthesise from γ-piperidinones the cyanohydrins (XXIV) and from the latter the hydroxy-acids (XXV) and their esters involving the carboxy-group [compounds (XXVI)] and the hydroxy-group [compounds (XXVII)].[65–71] Pinacones of the piperidine series—4-aryl(diaryl)-4-hydroxypiperidylmethanols[72]—have been obtained from γ-alkoxycarbonyl-γ-hydroxypiperidines and their pinacoline rearrangement to γ-acyl-γ-arylpiperidines has been carried out[73]. The conversion of γ-piperidinone cyanohydrins into γ-dialkylamino-γ-cyanopiperidines has been described and the latter have been converted into γ-dialkylaminopiperidines and γ-alkyl (aryl)piperidines[74,75]. γ-Amino-γ-carboxypiperidines (XXIX) have been obtained both from γ-amino-γ-cyanopiperidines (XXVIII)[76] and from γ-carboxy-γ-hydroxypiperidines (XXV).[77]

The second group of reactions of γ-piperidinones consists of their condensation reactions (Scheme 3). When γ-piperidinones (I) are condensed with benzaldehyde, both 3-benzylidene-[compounds (XXX)] and 3,5-dibenzylidene-derivatives [compounds (XXXI)] are formed[78–82]. Similar condensations with various aromatic aldehydes, including heterocyclic aldehydes, have been described[83–85]. 1-Acetyl-3-methoxycarbonyl-2,5-dimethyl-4-piperidinone (XXXII) has been obtained by the condensation of the corresponding piperidinone with dimethyl carbonate in the presence of sodium ethoxide[86]. The condensation of 1,2,5-trimethyl-4-piperidinone with formaldehyde, resulting in the 3-hydroxymethyl derivative (XXXIII) of this piperidinone, has been achieved[87]. 3-Dialkylaminomethyl-4-piperidinones (XXXIV) have been obtained by the Mannich condensation of γ-piperidinones[88–90]. Ethyl β-(3-ethoxycarbonyl-1-methyl-4-oxo-3-piperidyl)propionate (XXXV) has been obtained from 3-ethoxycarbonyl-1-methyl-4-piperidinone and ethyl acrylate in the presence of sodium hydride[58,91].

The cyanoethylation of γ-piperidinones with alkyl substituents in the β-position, which leads to the formation of β-alkyl-β-cyanoethyl-γ-piperidinones (XXXVI), has been described[92–95]. Further cyanoethylation of such piperidinones yielded $\beta\beta'$-di-(2-cyanoethyl)- and $\beta\beta\beta'$-tri-(2-cyanoethyl)-γ-piperidinones[96]. The condensation of 1,2,5-trimethyl-4-piperidinone (as well as its *N*-unsubstituted analogue) with bis-(β-methylvinyl) ketone leads to

Scheme 2



the formation of 1,2,5-trimethyl-5-(5-methyl-3-oxohex-4-en-1-yl)-4-piperidinone (XXXVII).[97] When 2,5-dimethyl-4-piperidinone was condensed with α-vinylpyridine in the presence of sodium, 2,5-dimethyl-5-[β-(2-pyridyl)-ethyl]-4-piperidinone (XXXVIII) was obtained[98].

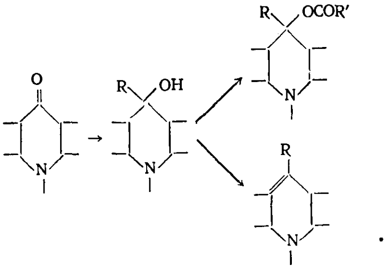
Treatment of 1-alkoxy-3-methoxycarbonyl-4-piperidinones with methyl iodide in the presence of sodium ethoxide yields 1-alkoxy-3-methoxycarbonyl-3-methyl-4-piperidinones[99]. The synthesis of 3-allyl-1-benzyl-4-piperidinone by alkylating 1-benzyl-4-piperidinone with allyl bromide after its preliminary treatment with sodium t-butoxide has been described[100]. Similar alkylation of γ-piperidinones has been described in another communication[55]. Treatment of 3-ethoxycarbonyl-1-methyl-4-piperidinone with benzyldimethylphenylammonium chloride and with allyldimethylphenylammonium bromide followed by hydrolysis and decarboxylation of the alkylation products yielded 3-benzyl(allyl)-1-methyl-4-piperidinones[101]. 1-Benzoyl-3-ethoxycarbonyl-3-propargyl-4-piperidinone (XXXIX) has been obtained from 1-benzoyl-3-ethoxycarbonyl-4-piperidinone and propargyl bromide[47].

Iminoxy-radicals (free radicals), which are chemically based on triacetoneamine and its derivatives substituted in the γ-position, occupy an independent place in the chemistry of γ-piperidinones[102-104].

II. SYNTHESES OF PHYSIOLOGICALLY ACTIVE PIPERIDINE DERIVATIVES FROM γ-PIPERIDINONES

The first physiologically active piperidine derivatives described, including medicinal drugs, consisted of esters of secondary γ-piperidinols. More than 80 reports have been published in which the reduction of γ-piperidinones to γ-piperidinols by various methods and their esterification are described. Some of the esters exhibit physiological activity, but have not found applications for different reasons. α-Eucaine (4-benzoyloxy-4-methoxycarbonyl-1,2,2,6,6-pentamethylpiperidine) and β-eucaine (4-benzoyloxy-2,2,6-trimethylpiperidine), which are powerful anaesthetics but exhibit an undesirable secondary activity, as well as a mydriatic preparation eucatropine (euphthalmine) (the ester of 1,2,2,6-tetramethyl-4-piperidinol and mandelic acid) are nowadays only of historical interest.

The esters of tertiary γ-piperidinols proved to be piperidine derivatives, obtainable from γ-piperidinones, which are important from the practical point of view. Various methods have been used to synthesis γ-hydroxy-derivatives with a tertiary hydroxy-group from γ-piperidinones; one of these involves the preparation of γ-piperidinols with the aid of organomagnesium and organolithium compounds[12,18,19,23,58,60,99-101,105-176]. Certain tertiary γ-piperidinols have been obtained from γ-piperidinones by the Reformatskii reaction[177,178]. The condensation of γ-piperidinones with ketones in the presence of ion-exchange resins, which results in the formation of tertiary γ-piperidinols containing β-hydroxyalkyl groups in the 4-position, has been described[179]:

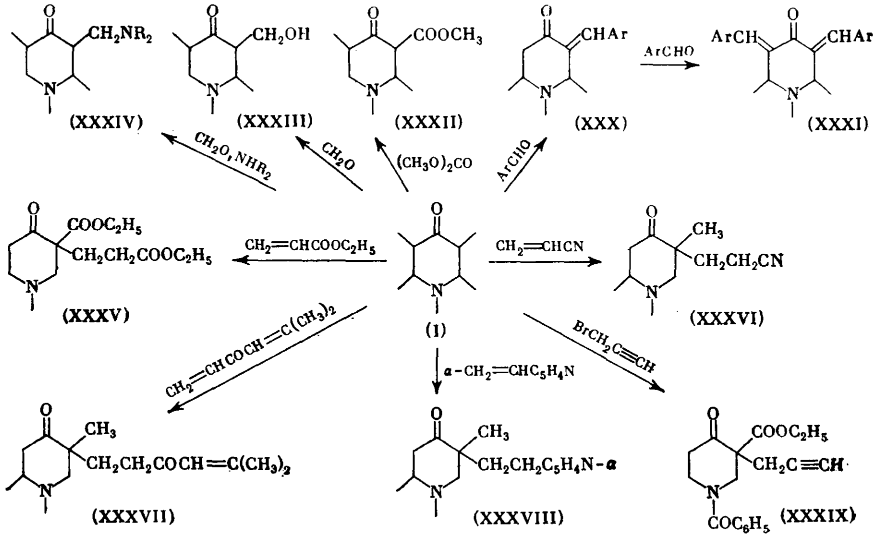


Many of the γ-piperidinols synthesised have been isolated in the form of individual isomers. Apart from the esterification of tertiary γ-piperidinols in order to obtain pharmacologically active compounds[18,19,99-101,105-109,112,114,116,117,120-122,124-126,128,129,131-133,135-137,139,142,146,148,150,155,158,167,170-175,180-197], their dehydration has also been studied, mainly in connection with the determination of the configurations of γ-piperidinols and the synthesis of piperidines which were used in the syntheses of pyridine bases[107,110,113,115,117,127,144-147,151,156,157,162,168,176,178,198-205].

The syntheses of tertiary γ-piperidinols and their esters have been carried out on a large scale. Effective analgesics have been found amongst them.

The ethers of tertiary γ-piperidinols have been inadequately investigated, partly due to certain difficulties in their synthesis. A method has been developed for the conversion of the esters of such alcohols into ethers by heating them with an excess of hydrogen chloride in an

Scheme 3



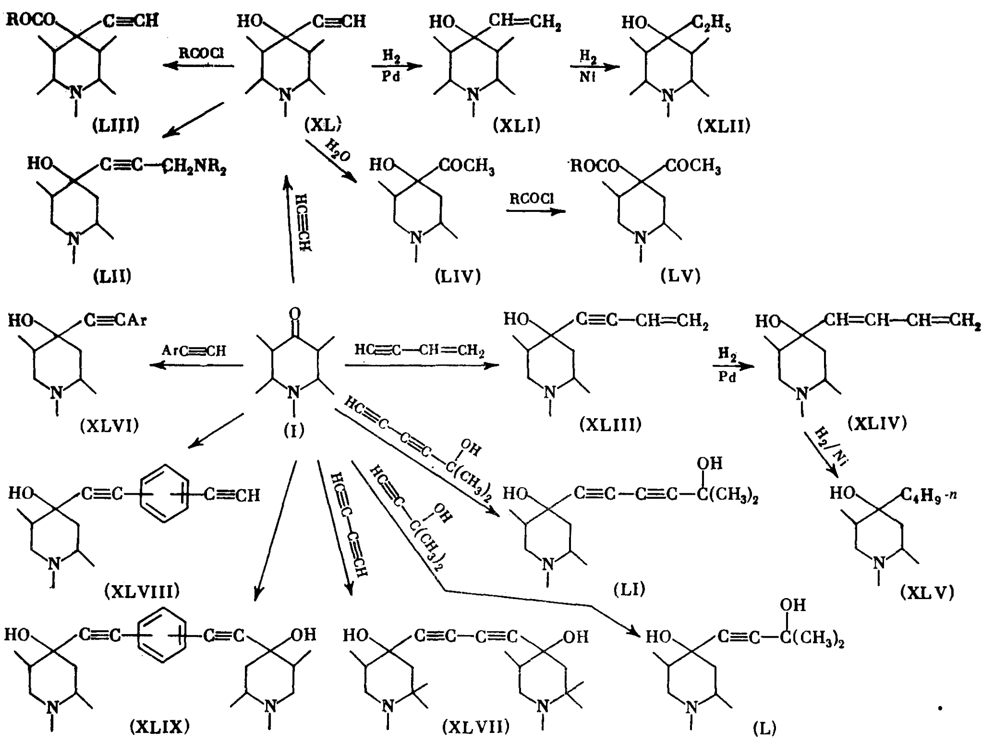
alcoholic solution. Thus 1-benzyl-4-ethoxy-4-α-furyl-3-methylpiperidine, which exhibits a considerable analgesic activity, has been obtained from 1-benzyl-4-α-furyl-3-methyl-4-propionyloxypiperidine[141,206,207]. The cyanoethylation of tertiary γ-piperidinols in the presence of potassium hydroxide leads to the formation of γ-(2-cyanoethoxy)piperidines[208]. The condensation of γ-piperidinones with acetylenic compounds has been carried out by familiar methods (Scheme 4). Many 4-ethynyl-4-piperidinols (XL) have obtained from γ-piperidinones (I), with various substituents in the ring and at the nitrogen atom, by condensation with acetylene; in many instances isomeric piperidinols were isolated and their steric structures established. Partial [to γ-vinylpiperidinols (XLI)] and complete to [γ-ethylpiperidinols (XLII)] hydrogenation of the ethynyl group has been achieved[69,112,180,184,209-233]. 4-Vinylethynylpiperidinols (XLIII) have been synthesised by condensing γ-piperidinones with vinylacetylene or vinylethynylmagnesium bromide. Partial [to piperidinols (XLIV)] and complete [to piperidinols (XLV)] hydrogenation of the vinylethynyl group has been achieved[112,114,234]. Analogous condensations of γ-piperidinones have been carried out with phenylacetylene[117,146,225,235,236] and naphthylacetylenes[237] [the synthesis of the piperidinols (XLVI)]. 4-Butadiynyl-4-piperidinols have been synthesised by the Chodkiewicz–Cadiot method from 4-ethynyl-4-piperidinols and bromo-derivatives of monosubstituted acetylenes[238]. The condensation of 2,2,5-trimethyl-4-piperidinone with diacetylene yielded a diacetylenic glycol—di-(4-hydroxy-2,2,5-trimethyl-4-piperidyl)-diacetylene (XLVII). An analogous glycol was obtained by the oxidative dimerisation of individual isomers from 4-ethynyl-1,2,5-trimethyl-4-piperidinol and was then hydrogenated[232,239,240]. Similar glycols have also been described[218].

Diethynylbenzenes with the ethynyl groups and other substituents in different positions in the benzene ring have been condensed with 1,2,5-trimethyl-4-piperidinone and condensation products involving both one [compounds (XLVIII)][238,241] and two [compounds (XLIX)][241,242] ethynyl groups have been obtained. The condensation of 1,2,5-trimethyl-4-piperidinone with ethynyldimethylmethanol [the synthesis of the glycol (L)][243] and of 2,5-dimethyl-4-piperidinone with diethynyldimethylmethanol [the synthesis of the glycol (LI)][219] have been achieved.

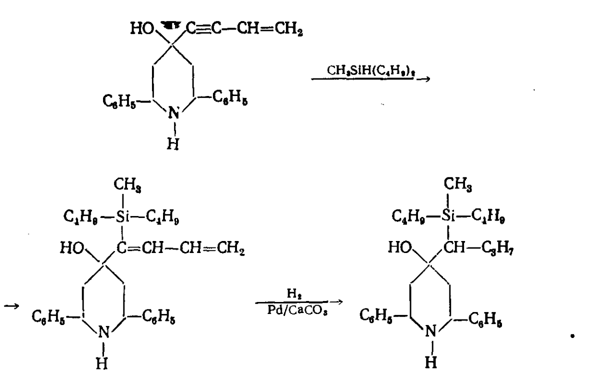
A large number of dialkylaminomethylethynyl derivatives (LII) of acetylenic piperidinols (XL) with terminal acetylenic hydrogen have been synthesised from the latter by the Mannich method[193,217,224,231,244-249]. The condensation of acetylenic piperidinols with ketones[250] and the cyanoethylation of the resulting glycols have been investigated[251]. The esters (LIII) of the acetylenic alcohols (XL) have been obtained and the triple bond has been hydrated [the synthesis of 4-acetyl-4-piperidinols (LIV) and their esters (LV)] and a number of other reactions involving the ethynyl group have been carried out[69,71,146,213,216,221,223,231,238,252-263]. The aminomethylation[264] and cyanoethylation[265-267] of acetylenic γ-piperidinols at the hydroxy-group as well as the preparation of their carbamates have been described. 4-Vinyl-4-piperidinols, obtained by the partial hydrogenation of 4-ethynyl-4-piperidinols by oxidation with hydrogen peroxide, have been converted into 4-epoxy-4-hydroxy-derivatives of piperidine.

Only limited studies have been made of the synthesis of silicon-containing piperidine derivatives, including tertiary γ-piperidinols. When 2,6-diphenyl-4-vinylethynyl-4-piperidinol was treated with dibutylmethylsilane in the presence of a Spier catalyst, 4-(1-dibutylmethylsilylbuta-1,3-dienyl)-2,6-diphenyl-4-piperidinol was

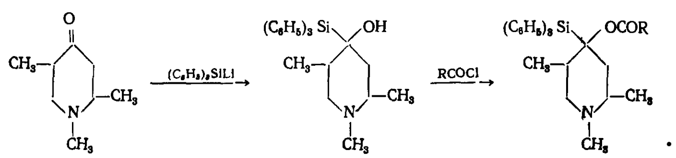
Scheme 4



isolated and then converted by hydrogenation into 4-(1-dibutylmethylsilyl-1-butyl)-2,6-diphenyl-4-piperidinol. An analogous reaction has been carried out with 1,2,5-trimethyl-4-vinylethynyl-4-piperidinol[268]:



Another example is provided by the synthesis of the isomeric 1,2,5-trimethyl-4-triphenylsilyl-4-piperidinols and their esters from 1,2,5-trimethyl-4-piperidinone and triphenylsilyl-lithium[269]:

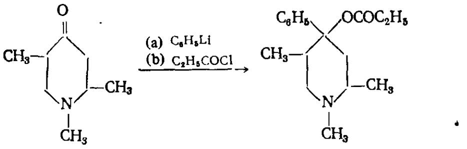


Pharmacological study of secondary and tertiary γ-piperidinols has shown that they are as a rule physiologically inactive. The analgesic activity of the isomeric 1,2,5-trimethyl-4-phenyl-4-piperidinols has been erroneously reported[270]. However, tertiary γ-piperidinols include the neuroplegic preparation 4-*p*-chlorophenyl-1-(3-benzoyl-1-fluoropropionyl)-4-piperidinol. According to preliminary data[269], 1,2,5-trimethyl-4-triphenylsilyl-4-piperidinol exhibits a bactericidal activity.

The most active analgesics proved to be the esters of propionic acid and tertiary γ-piperidinols with a phenyl substituent in the 4-position. Two of these preparations have been introduced into medical practice, namely prodine (α-prodine, Nisentil, anedol) and promedol, and have found extensive applications and have significantly limited the use of morphine as an analgesic.

Prodine (the hydrochloride of 1,3-dimethyl-4-phenyl-4-propionyloxypiperidine) was obtained as follows. The cyclisation of (β-methoxycarbonylethyl)-(β-methoxycarbonylpropyl)methylamine results in the formation of 5-methoxycarbonyl-1,3-dimethyl-4-piperidinone, from which 1,3-dimethyl-4-piperidinone is formed after hydrolysis and decarboxylation[271]. The reaction of this piperidinone with phenyl-lithium yielded a mixture of isomeric 1,3-dimethyl-4-phenyl-4-piperidinols and then the propionate esters of both isomers (α-prodine and β-prodine)[109]. The high analgesic activity of prodine has been reported[105]. The synthesis of compounds analogous to prodine has been described in reports of independent investigations[108,110].

1,2,5-Trimethyl-4-piperidinone is used in the synthesis of promedol (the hydrochloride of 1,2,5-trimethyl-4-phenyl-4-propionyloxypiperidine)[116,272]. In the technique employed promedol is obtained without isolating 1,2,5-trimethyl-4-phenyl-4-piperidinol by treating with propionyl chloride the lithium alkoxide derived from this alcohol:



The following method is more rational: synthesis of 1,2,5-trimethyl-4-phenyl-4-piperidinol, isolation (crystallisation and chromatographic separation) of the γ-isomer from the mixture of isomers, and esterification of the γ-isomer (yield more than 90%) with propionic anhydride in the presence of pyridine.

III. THE STERIC STRUCTURES OF CERTAIN TERTIARY γ-PIPERIDINOLS

Numerous studies have been devoted to the stereochemistry of secondary and tertiary γ-piperidinols. Studies of this kind are being vigorously continued also at the present time. In this review our aim is to examine research in this field associated with the chemistry of γ-piperidinols. This was done to some extent in a previous review[273], but the latter has already become obsolete.

We shall consider only studies associated with the investigation of the configurations and conformations of isomeric 1,3-dimethyl-4-phenyl-4-piperidinols and 1,2,5-trimethyl-4-phenyl-4-piperidinols. The choice of these compounds is dictated by several factors. In the first place, the γ-piperidinols are used as the starting materials in the syntheses of effective analgesic medicinal preparations—the isomeric prodines and the isomeric promedols. Among the numerous derivatives of γ-piperidinones, only these compounds have found extensive applications in medicinal practice. The conformational analysis of piperidine derivatives was initiated in studies undertaken to investigate the stereochemistry of the above piperidinols using in the first place chemical and then spectroscopic methods. Many workers who studied the structures of the isomeric prodines and promedols frequently reached contradictory conclusions. Whereas in the case of the isomeric 1,3-dimethyl-4-phenyl-4-piperidinols these contradictions were fairly rapidly eliminated, in the case of the 1,2,5-trimethyl analogues they accumulated in the course of time, which not only interfered with the solution of this specific problem but to some extent inhibited the development of the conformational analysis of piperidine systems. Unfortunately the authors who categorically adhered to an erroneous treatment of the mixture of isomeric 1,2,5-trimethyl-4-phenyl-4-piperidinols[270,274] later changed their views without reporting any reasons for the earlier incorrect conclusions[261,275].

The preparation of a mixture of isomeric 1,3-dimethyl-4-phenyl-4-piperidinols and the hydrochlorides of their propionates—the α-isomer (m.p. 212–214°C; 220–221°C according to other data[125]) and the β-isomer (m.p. 190 to 192°C; 195–196°C according to other data[125])—was first reported by Ziering and Lee[109], who also presented the experimental results for the isolation of the enantiomers of β-prodine with the aid of D-tartaric and L-malic acids. The diastereoisomers of 1,3-dimethyl-4-phenyl-4-piperidinol were designated as α-form (m.p. 100–101°C) and the β-form (m.p. 116–118°C) (the hydrochlorides of the corresponding propionates were indicated above). The following configuration, later shown to be erroneous, was initially attributed to them (on the basis of infrared spectroscopic data alone[276]): *cis*-disposition of the methyl group at $C_{(3)}$ and of the phenyl group at $C_{(4)}$ for the α-form and *trans*-disposition of the same substituents for the β-form[109,124]. Erroneous configurations were also assigned to structural analogues of the above α- and β-forms of piperidinols containing substituents other than the methyl group at $C_{(3)}$. The fact that these conclusions concerning structure, for example, for the α- and β-isomers of 3-allyl-1-methyl-4-phenyl-4-piperidinols[124], were unsound was demonstrated by Bell and Portoghese[60].

The problem of the configurations and conformations of the α- and β-isomers of 1,3-dimethyl-4-phenyl-4-piperidinols was solved initially by chemical and then by spectroscopic methods. The steric structures of the α- and β-isomers of 1,3-dimethyl-4-phenyl-4-piperidinols and their analogues (the α- and β-series), with other substituents at the nitrogen and $C_{(3)}$ atoms, were studied in a number of investigations. It was established that the proportion of piperidinols of the α-series is much greater than that of the compounds of the β-series owing to more favourable steric conditions for the formation of the former with the *trans*-disposition of the substituent at $C_{(4)}$ relative to that at $C_{(3)}$. The esters of the β-isomers of piperidinols hydrolyse at a higher rate than those of the α-isomers[277] and the β-isomers are more readily esterified than the α-isomers (axial hydroxy-group). The interaction of β-isomers of piperidinols with thionyl chloride involves the exchange of the hydroxy-group for chlorine, while the reaction of the α-isomers involves mainly dehydrochlorination. On the basis of these data, it was concluded initially that the α-isomer of the piperidinol corresponding to prodine has the structure of 1,3*e*-dimethyl-4*e*-phenyl-4-piperidinol[136,278,279]. It was established that the α- and β-isomers of piperidinols have infrared spectra with characteristic features[125].

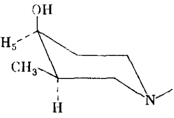
X-Ray diffraction analysis of α-prodine (the hydrochloride of the propionate of the α-isomer of 1,3-dimethyl-4-phenyl-4-piperidinol) showed that its molecule has the "chair" conformation with the phenyl group in the equatorial position, while the methyl group at $C_{(3)}$ is in the *trans*-position relative to the phenyl group at $C_{(4)}$.[280,281] X-Ray diffraction study of the hydrobromide and hydrochloride of β-prodine led to the conclusion that its molecule also has "chair" conformation, and that the methyl group at $C_{(3)}$ and the equatorial phenyl group are in the *cis*-positions[282-284]. An analogous conclusion about the configurations and conformations of the α-isomer of 1,3-dimethyl-4-phenyl-4-piperidinol (the CH_3 and equatorial C_6H_5 groups in the *trans*-position) and the β-isomer (the CH_3 and equatorial C_6H_5 groups in the *cis*-position) was reached on the basis of a study of their ^{1}H NMR spectra[150,285-288] as well as the spectra of their esters[289].

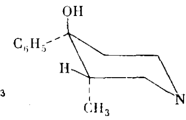
The results obtained in a study of the products of the dehydration of the isomeric α- and β-1,3-dimethyl-4-phenyl-4-piperidinols under the conditions of acid catalysis (*trans*-elimination, E2 mechanism) were also used to demonstrate the configurations of these piperidinols. Dehydration of the β-isomer under comparable conditions leads to the formation of 1,5-dimethyl-4-phenyl-1,2,5,6-tetrahydropyridine, while dehydration of the α-isomer results in the formation of approximately equal amounts of 1,3-dimethyl-4-phenyl, and 1,5-dimethyl-4-phenyl-1,2,5,6-tetrahydropyridines[151]. The same results were obtained in a study of the dehydration of the 4-*o*-tolyl analogues of the α- and β-isomers of this piperidinol[162].

The synthesis of the enantiomers of the α-isomer of 1,3-dimethyl-4-phenyl-4-piperidinol from the enantiomers of 3-allyl-1-methyl-4-phenyl-4-piperidinol has been achieved. Treatment of the optical isomers of this piperidinol with osmium tetroxide and then with sodium periodate yielded the enantiomers of the 3-formylmethyl derivative, which was isolated in the form of hemiacetals. Decarbonylation of the latter yielded the enantiomers of the α-isomer of 1,3-dimethyl-4-phenyl-4-piperidinol $\{[\alpha]_D = +5.6$ and $[\alpha]_D = -5.8\}$.[290] The synthesis of α- and β-prodines (hydrochlorides) labelled with tritium in the phenyl group and the isolation of their optical isomers have been described. The following characteristics of the optical isomers were obtained:

(+)-[^{3}H] C_6H_5-α — m.p. 190—191°, $[\alpha]_D = +35.3°$;
(—)-[^{3}H] C_6H_5-α — m.p. 194—195°, $[\alpha]_D = -37.5°$;
(+)-[^{3}H] C_6H_5-β — m.p. 185—186°, $[\alpha]_D = +66.8°$;
(—)-[^{3}H] C_6H_5-β — m.p. 190—191°, $[\alpha]_D = -71°$.

The separation of the isomeric piperidinols into their enantiomers, which were subsequently propionylated, was achieved with the aid of tartaric and dibenzoyltartaric acids. It was established that the (+)-enantiomers are more active analgesics than the (−)-enantiomers[172,291]. Thus (+)-α-prodine is 25 times more active than (−)-α-prodine; the analogous β-prodines have activities differing by a factor of 13.[292] Thus one may assume that the problem of the configurations and conformations of the α- and β-isomers of 1,3-dimethyl-4-phenyl-4-piperidinols has been solved[293].


α-isomer


β-isomer

The problem of elucidating the steric structures of the three isomeric 1,2,5-trimethyl-4-phenyl-4-piperidinols, which are formed when 1,2,5-trimethyl-4-piperidinone reacts with phenyl-lithium, is more complex: the α-isomer (m.p. 106−107°C) from which α-promedol is derived (its analgesic activity is higher than that of morphine approximately by a factor of 4−6), the β-isomer (m.p. 102−103°C) from which isopromedol is derived (more active than promedol by a factor of 2−3), and the γ-isomer (m.p. 107−108°C) from which promedol is derived (more active than morphine by a factor of 2−3).[116] The racemic promedol was resolved into enantiomers; it was established that the (+)-enantiomer is approximately 9 times more active than the (−)-enantiomer[175]. The formation of only these three isomeric piperidinols has now been established by careful and repeated studies of the products of the reaction of 1,2,5-trimethyl-4-piperidinone with phenyl-lithium.

The existence of two isomers (*trans*- and *cis*- with respect to the methyl groups at $C_{(2)}$ and $C_{(5)}$ in 1,2,5-trimethyl-4-piperidinone) gave rise to no doubts, because interaction of this piperidinone with phenyl-lithium leads to the formation of three isomeric 1,2,5-trimethyl-4-phenyl-4-piperidinols. Experimental study of the isomerism of this piperidinone, which confirmed its existence in the *trans*- and *cis*-forms with the former, containing equatorial methyl groups, greatly predominating, was carried out with the aid of its ^{1}H NMR spectrum and the exchange of α-protons for deuterium[294]. The isolation of the *trans*-isomer of 1,2,5-trimethyl-4-piperidinone has been described[130].

In one of the first studies[127] associated with the solution of the problem of the configurations and conformations of the α- and γ-isomers of 1,2,5-trimethyl-4-phenyl-4-piperidinone chemical methods were used. The α- and γ-isomers of 2,5-dimethyl-, 1,2,5-trimethyl-, and 1-acetyl-2,5-dimethyl-4-phenyl-4-piperidinols were synthesised and related to one another by the usual transformations. The γ-isomers greatly predominated in the synthesis of the first two piperidinols. Since the N $\rightleftharpoons$ O acyl migration takes place in the γ-isomer of 1-acetyl-2,5-dimethyl-4-phenyl-4-piperidinol, it was concluded that the hydroxy-group in this isomer is in the axial position. In the α-isomer the N → O acyl migration takes place under more severe conditions with inversion of the configuration at $C_{(4)}$, since the same acetoxy-derivative is formed as from the γ-isomer. These transformations indicate the identical *trans*-equatorial dispositions of the methyl groups at $C_{(2)}$ and $C_{(5)}$ (the most favourable conformation for both the initial piperidinone and the piperidinols) in the α- and γ-isomers and of the equatorial disposition of the hydroxy-group in the α-isomer.

The same conclusion was reached in a study of the chromatographic mobilities of the γ- and α-isomers of 1,2,5-trimethyl-4-phenyl-4-piperidinol[295]. An analogous relation has been established for the γ- and α-isomers of 1,2,5-trimethyl-4-*m*-tolyl-4-piperidinol[157]. A quantitative study has been made[296] of the esterification of the α- and γ-isomers of 1,2,5-trimethyl-4-phenyl-4-piperidinol and it has been shown that the α-isomer, with the equatorial hydroxy-group, is esterified much faster than the γ-isomer. The same behaviour has been established in a study of the hydrolysis of the esters of both these isomeric piperidinols.

The infrared spectra of the γ- and β-isomers of 1,2,5-trimethyl-4-phenyl-4-piperidinol have the same characteristics as the spectra of the analogous 3-alkyl-4-aryl-4-piperidinols with the *trans*-disposition of the alkyl and aryl groups[200].

The configuration of the α-isomer of 1,2,5-trimethyl-4-phenyl-4-piperidinol has been indirectly confirmed[273,289,297]. Since β-prodine and α-promedol have almost the same analgesic activities in the series of the isomeric prodines and promedols, it has been suggested that they have the same *cis*-configurations of the CH_3 group in the β-position and the C_6H_5 group in the γ-position, which proved to be true.

Erroneous conclusions about the configurations and conformations of the isomeric α-, β-, and γ-1,2,5-trimethyl-4-phenyl-4-piperidinols were reached[270]. Unfortunately, in order to determine the steric structures of these isomers, the authors confined themselves to the results of qualitative esterification and dehydration experiments, which could not serve as a basis for the solution of conformational problems. The structure of 1,2*e*,5*e*-trimethyl-4*e*-phenyl-4-piperidinol was attributed to the α-isomer (m.p.106–107°C), which is actually 1,2*e*,5*e*-trimethyl-4*a*-phenyl-4-piperidinol, the structure of 1,2*a*,5*e*-trimethyl-4**a**-phenyl-4-piperidinol was attributed to the β-isomer (m.p. 102–103°C), which is actually 1,2*a*,5*e*-trimethyl-4*e*-phenyl-4-piperidinol, and the structure of 1,2*e*,5*e*-trimethyl-4*a*-phenyl-4-piperidinol was attributed to the γ-isomer (m.p. 107–108°C), which is actually 1,2*e*,5*e*-trimethyl-4*e*-phenyl-4-piperidinol. Shvetsov and Kucherov[270] also failed to take into account the published experimental data[127] concerning the determination of the structures of the isomeric 1,2,5-trimethyl-4-phenyl-4-piperidinols. In estimating the rates of esterification of γ-piperidinols isomeric at $C_{(4)}$ conclusions inconsistent with the fundamental principles of conformational analysis were reached[196,298]. Solely on the basis of "qualitative" observations, it was concluded erroneously that "the axially oriented hydroxy-group is more readily esterified ... than the equatorial hydroxyl"[196]. This conclusion conflicts with the above quantitative data for the esterification of the α- and γ-isomers of 1,2,5-trimethyl-4-phenyl-4-piperidinol[296].

Erroneous conclusions about the structures of the promedol and α-promedol piperidinols were reached in a study[274] related to a series of previous investigations[72,212,253]. Since the compounds to which the authors[274] related the steric structures of the α- and γ-isomers of 1,2,5-trimethyl-4-phenyl-4-piperidinol are the isomeric 4-ethynyl-1,2,5-trimethyl-4-piperidinols and 4-cyano-4-hydroxy-1,2,5-trimethylpiperidines, we need point out the erroneous conclusions concerning these compounds only, leaving aside other compounds described (the authors'[274] ideas about the steric structures of these compounds have now changed). The structure with the *cis*-disposition of the methyl group at $C_{(3)}$ and of the ethynyl group at $C_{(4)}$ was attributed arbitrarily[274] to the γ-isomer (m.p. 177 to 178°C) of 4-ethynyl-1,2,5-trimethyl-4-piperidinol. On the basis of chromatographic data alone, this conclusion was amended[299] and the structure with the *trans*-disposition of the same substituents was attributed to the above compound. Thus the conclusions concerning the steric structures of many derivatives of γ-piperidinols, including the isomeric 1,2,5-trimethyl-4-phenyl-4-piperidinols[72,212,253,274], were erroneous.

Shvetsov et al.[274] converted the γ-isomer of 4-cyano-1,2,5-trimethyl-4-piperidinol (m.p. 141–143°C) into the γ-isomer of 1,2,5-trimethyl-4-phenyl-4-piperidinol. However, since the erroneous configuration with the *cis*-disposition of the methyl group at $C_{(3)}$ and of the cyano-group at $C_{(4)}$ was attributed to the above cyanohydrin (later amended[275]), an erroneous conclusion was also reached about the structures of the isomeric 1,2,5-trimethyl-4-phenyl-4-piperidinols.

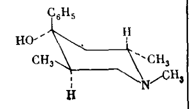
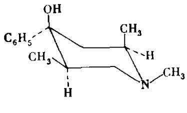
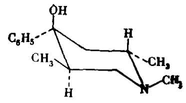
Subsequent studies confirmed the conclusions about the steric structures of the promedol alcohols arrived at by Prostakov and coworkers[127,273]. X-Ray diffraction of the α- and γ-isomers of 1,2,5-trimethyl-4-phenyl-4-piperidinol confirmed the *trans*-equatorial disposition of their methyl groups at $C_{(2)}$ and $C_{(5)}$ as well as the axial disposition of the phenyl group in the α-isomer and its equatorial disposition in the γ-isomer[300].

These conclusions[127,273] about the configurations and conformations of the α- and γ-isomers and also about the configuration of the β-isomer of 1,2,5-trimethyl-4-phenyl-4-piperidinol were fully confirmed in a study[301] based on infrared and ^{1}H NMR spectroscopic data. The inverted form, proposed previously by Prostakov and Mikheeva[273], was established for the conformation of the β-isomer. The occurrence of the chair–boat equilibrium, with the chair conformation predominating, was also demonstrated in solutions of the α- and β-isomers.

The ratio of the conformers of the isomeric promedols in solution was estimated from the difference between the free energies of the conformations with axial and equatorial phenyl groups. It follows from this estimate that conformers with the axial phenyl group constitute 97% of the α-isomer (alphapromedol, $\Delta F = -2.1$ kcal mole^{-1}), 62% of the β-isomer (isopromedol, $\Delta F = -0.3$ kcal mole^{-1}), while the corresponding conformer of the γ-isomer (promedol, $\Delta F = +7$ kcal mole^{-1}) does not exist[302].

By analysing ^{13}C NMR spectra, taking into account earlier studies, the following conclusions have been reached[303] about the structures of the isomeric 1,2,5-trimethyl-4-phenyl-4-piperidinols and their esters. The tentative conformations in deuterochloro-form are: α-isomer—1,2*e*,5*e*-trimethyl-4*a*-phenyl-4-piperidinol (the substance has the same conformation in the solid state); β-isomer—1,2*a*,5*e*-trimethyl-4*e*-phenyl-4-piperidinol; γ-isomer—1,2*e*,5*e*-trimethyl-4*e*-phenyl-4-piperidinol:(the substance has the same conformation in the solid state). The Table presents data for the true conformations of the isomers of 1,2,5-trimethyl-4-phenyl-4-piperidinol.

The configurations and conformations of the isomers of 1,2,5-trimethyl-4-phenyl-4-piperidinols.

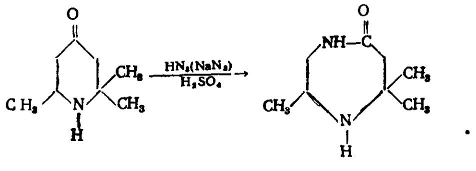
Isomer	M.p., °C (Ref.116)	Structure of isomers	Studies in which their structure has been proved	Studies in which erroneous conclusions about the structures were reached
α	106—107		127,273,295,296, 297*,300*,301, 303*,304	270, 274
β	102—103		200***,301,303**	143, 270
γ	107—108		127,273,295,296, 300,301,303—306	270, 274

*Designated by the authors as the β-isomer[205,303].
**Designated by the authors as the α-isomer[205,303].
***Configuration.

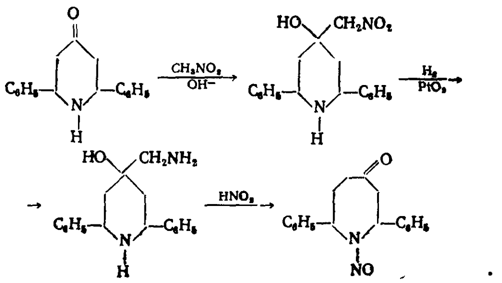
Thus, one may assume that the problems concerning the structures of γ-piperidinols, constituting the basis of effective analgesics, which has been discussed for many years, sometimes from opposed standpoints, have now been solved and that the conformational analysis of piperidine systems is now a fairly established part of the chemistry of nitrogen-containing heterocycles.

IV. γ-PIPERIDINONES IN SYNTHESES OF HETEROCYCLIC COMPOUNDS

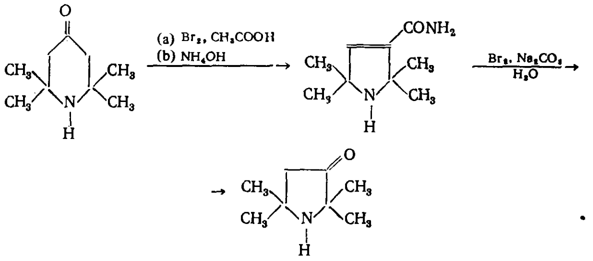
γ-Piperidinones are widely used in the syntheses of various heterocyclic compounds. Several examples of reactions of γ-piperidinones involving ring expansion have been described. 2,2,6-Trimethyl-4-piperidinone has been converted by the Schmidt reaction into 2,7,7-trimethyl-5-homopiperazinone:



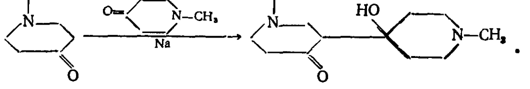
Analogous transformations have been achieved also for other γ-piperidinones[307–309]. The condensation of 2,6-diphenyl-4-piperidinone with nitromethane yielded 4-nitromethyl-2,6-diphenyl-4-piperidinol, which was reduced to 4-aminomethyl-2,6-diphenyl-4-piperidinol. Treatment of the latter with nitrous acid leads to the formation of 1-nitroso-2,7-diphenyl-1-aza-4-cycloheptanone[9]:



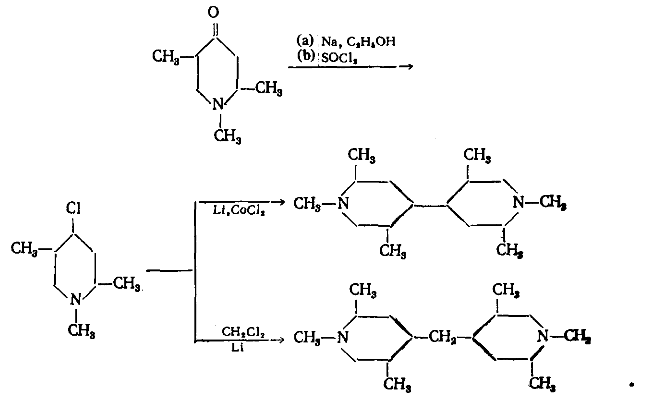
1-Benzyl-1-aza-3-cycloheptanone has been obtained from 1-benzyl-4-piperidinone by treating the latter with *N*-nitrosomethylurethane in the presence of barium oxide[310]. The synthesis of 2,2,5,5-tetramethyl-3-pyrrolidinone from triacetoneamine is an example of transformations of γ-piperidinones involving ring contraction. The amide of 2,2,5,5-tetramethyl-Δ^3-pyrrolinecarboxylic acid was obtained by treating with ammonia 3,3-dibromo-2,2,6,6-tetramethyl-4-piperidinone (formed on bromination of triacetoneamine) and was converted into a substituted 3-pyrrolidinone[311]:



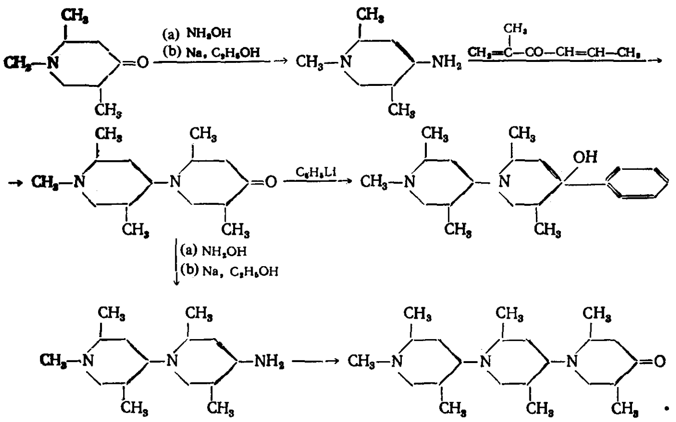
Several methods of synthesising di- and tri-piperidines from γ-piperidinones have been described. Intermolecular condensation of 1-methyl-4-piperidinone yielded a ketol—1-methyl-4-(1-methyl-4-oxo-3-piperidyl)-4-piperidinol[312]:



Bis(1,2,5-trimethyl-4-piperidyl) was obtained by treating 4-chloro-1,2,5-trimethylpiperidine with lithium or sodium in the presence of $CoCl_2$. Bis-(1,2,5-trimethyl-4-piperidyl)methane is formed from the same halogeno-derivative and methylene chloride in the presence of lithium[313]:

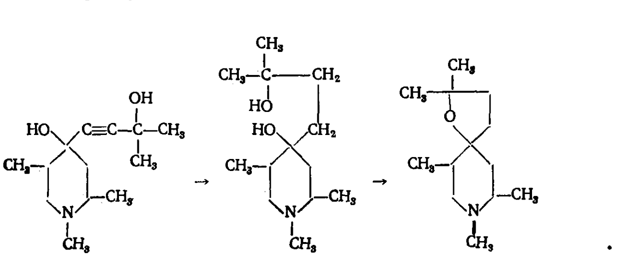


Condensation of 4-amino-1,2,5-trimethylpiperidine (obtained from the oxime of 1,2,5-trimethyl-4-piperidinone) with isopropenyl propenyl ketone yielded 2,5-dimethyl-1-(1,2,5-trimethyl-4-piperidyl)-4-piperidinone. Analogous transformations of this bicyclic system—the conversion of the oxo-group into an oxime group and then an amino-group and condensation of the resulting amine with isopropenyl propenyl ketone—led to the synthesis of terpiperidyl—2,5-dimethyl-4-(2,5-dimethyl-4-oxo-1-piperidyl)-1-(1,2,5-trimethyl-4-piperidyl)piperidine[153]:



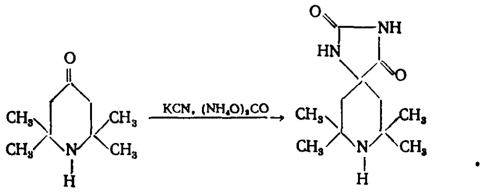
Synthesis of Spiro-compounds

The hydrogenation of 4-(3-hydroxy-3-methylbut-1-ynyl)-1,2,5-trimethyl-4-piperidinol (obtained by condensing 2,5-dimethyl-4-piperidinone with ethynyldimethylmethanol and subsequent N-methylation) results in the formation of a γ-glycol, the treatment of which with 10% sulphuric acid leads to its conversion into 2,2,7,8,10-pentamethyl-1-oxa-8-azaspiro[4,5]decane[243]:

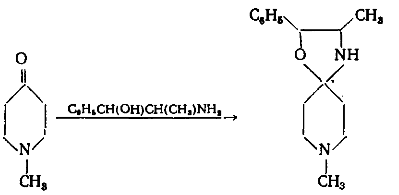


An analogous spiro-compound—2,2,7,10-tetramethyl-3-oxo-1-oxa-8-azaspiro[4,5]decane—is formed under the conditions of the hydration of the triple bond of 4-(3-hydroxy-3-methylbut-1-ynyl)-2,5-dimethyl-4-piperidinol[314]. Similar spiro-compounds have been described in other communications[315,316].

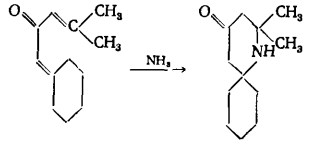
7,7,9,9-Tetramethyl-1,3,8-triazaspiro[4,5]decane-2,4-dione has been obtained from triacetoneamine, potassium cyanide, and ammonium carbonate. Analogous spiro-compounds have been synthesised from triacetoneamine substituted at the nitrogen atom[317] and also from 1,2,5-trimethyl-4-piperidinone cyanohydrin[318]. The syntheses of spirohydantoins, obtained from 1-alkyl-4-piperidinones, have been described[319,320]:



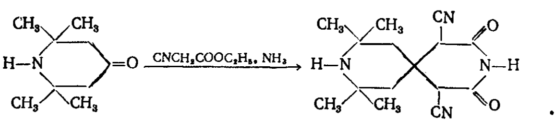
The condensation of 1-methyl-4-piperidinone with norephedrine leads to the formation of 3,8-dimethyl-2-phenyl-1-oxa-4,8-diazaspiro[4,5]decane[321]



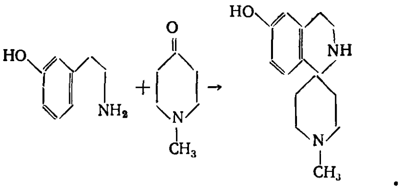
Analogous compounds substituted in the oxazolidine ring nitrogen have been described[322]. The reaction of the product of the condensation of mesityl oxide and cyclohexanone with ammonia (the method of synthesis of γ-piperidinones from divinyl ketones) yielded 2,2-dimethyl-4-oxo-1-azaspiro[5,5]undecane[323]:



The condensation of triacetoneamine with cyanoacetic ester and ammonia, resulting in the formation of 1,5-dicyano-8,8,10,10-tetramethyl-3,9-diazaspiro[5,5]-undecane-2,4-dione, has been achieved[324]:

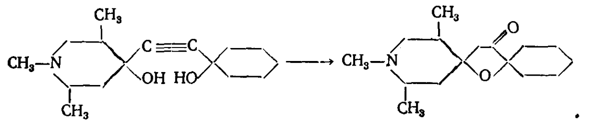


1′-Methyl-6-hydroxyspiro[1,2,3,4-tetrahydroisoquinoline-1,4′-piperidine] is formed when 3-(β-aminoethyl)-phenol is condensed with 1-methyl-4-piperidinone[325]:

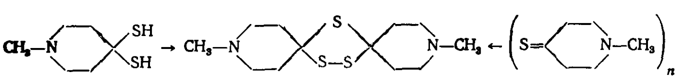


An analogous compound has been obtained from 2-amino-1-(3-hydroxyphenyl)ethanol[322].

The hydration of the triple bond of 4-[1-hydroxy-(1-cyclohexyl)ethynyl]-1,2,5-trimethyl-4-piperidinol involves the cyclodehydration of the resulting ketoglycol and leads to the formation of 1,3,4-trimethyl-14-oxo-7-oxa-3-azaspiro[5,1,5,2]pentadecane[252]:

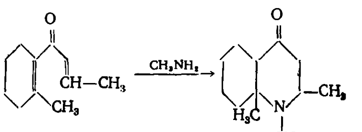


The crystallisation of the hydrochloride of 4,4-dimercapto-1-methylpiperidine and of the polymer of the hydrochloride of 1-methylthio-4-piperidinone (both substances have been obtained from 1-methyl-4-piperidinone) led to the isolation of the hydrochloride of dispiro-1,2,4-tritolane[45]:

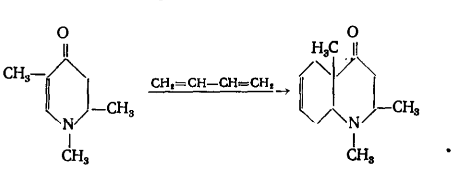


The Synthesis of Condensed Heterocyclic Compounds

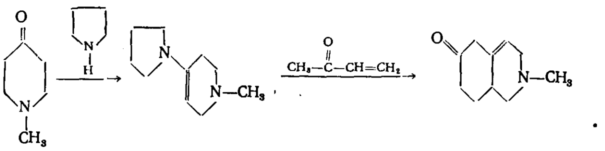
The method of synthesis of γ-piperidinones from divinyl ketones has been used to synthesise 1,2,8*a*-trimethyldecahydro-4-quinolinone, formed in the condensation of 2-methyl-Δ^1-cyclohexenyl propenyl ketone with methylamine[326]:



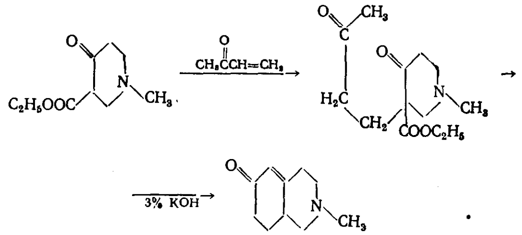
1,2,4*a*-trimethyl-1,2,3,4,4*a*,5,8,8*a*-octahydro-4-quinolinone is formed by the Diels–Alder reaction from 1,2,5-trimethyl-4-oxo-1,2,3,4-tetrahydropyridine (obtained from 1,2,5-trimethyl-4-piperidinone) and butadiene[327]:



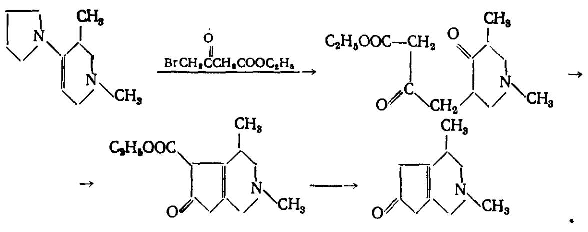
The condensation of 1-methyl-4-piperidinone with pyrrolidine results in the formation of 1-methyl-4-(1-pyrrolidinyl)-1,2,3,6-tetrahydropyridine, the reaction of which with methyl vinyl ketone gives 2-methyl-1,2,3,5,6,7,8,8*a*-octahydro-6-isoquinolinone[328]:



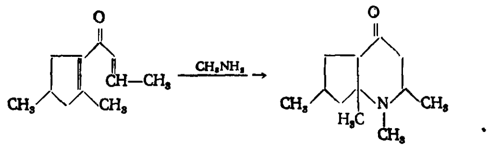
The condensation of 3-ethoxycarbonyl-1-methyl-4-piperidinone with methyl vinyl ketone has been used to synthesise 2-methyl-1,2,3,4,6,7,8,8*a*-octahydro-6-isoquinolinone[329]:



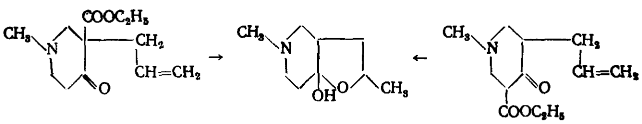
5-(γ-Ethoxycarbonyl-β-oxopropyl)-1,3-dimethyl-4-piperidinone, obtained from 1,5-dimethyl-4-(1-pyrrolidinyl)-1,2,3,6-tetrahydropyridine by cyclisation under the influence of potassium t-butoxide and subsequent decarboxylation of the condensation product, was converted into 2,4-dimethyl-2,3,4,5,6,7-hexahydro-1*H*-2-(6-pyrindinone)[47]:



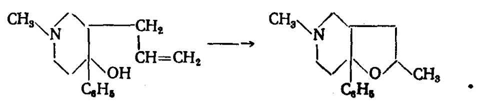
2,4-Dimethyl-Δ^1-cyclopentyl propenyl ketone (a divinyl ketone) reacts with methylamine and is converted into 1,2,6,7*a*-tetramethylperhydro-(4-pyrindinone)[326]:



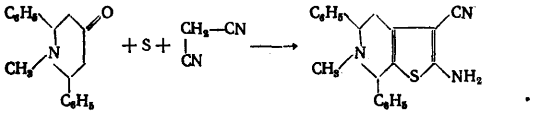
7*a*-Hydroxy-2,5-dimethylperhydrofuro[3,2-*c*]pyridine is formed on heating 3-allyl-3-ethoxycarbonyl-1-methyl-4-piperidinone as well as 3-allyl-5-ethoxycarbonyl-1-methyl-4-piperidinone with 20% hydrochloric acid. It is suggested that the removal of the ethoxycarbonyl group is accompanied by the simultaneous hydration of the double bond in the allyl group, which is followed by the formation of a hemiacetal[100,101]:



2,5-Dimethyl-6*a*-phenylperhydrofuro[3,2-*c*]pyridine was obtained under analogous conditions from 3-allyl-1-methyl-4-phenyl-4-piperidinol[100]:



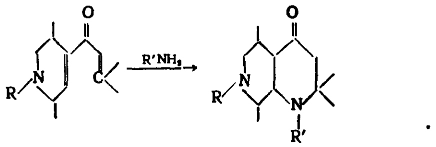
The condensation of 1-methyl-2,6-diphenyl-4-piperidinone with malonodinitrile in the presence of sulphur has been achieved and 2-amino-3-cyano-6-methyl-5,7-diphenyl-4,5,6,7-tetrahydrothieno[2,3-*c*]pyridine was obtained and was used in the synthesis of the condensed system of pyridothienopyrimidine[330]:



The analogous condensation of 1-(β-hydroxyethyl)-4-piperidinone with ethyl cyanoacetate and sulphur yielded 2-amino-3-ethoxycarbonyl-6-(β-hydroxyethyl)-4,5,6,7-tetrahydrothieno[2,3-*c*]pyridine[331].

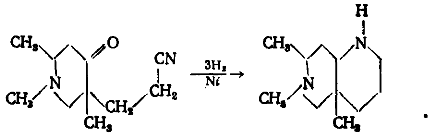
Synthesis of Fully or Partly Hydrogenated Naphthyridines

1,2,3,6-Tetrahydro-4-pyridyl vinyl ketones, substituted in the nitrogen-containing ring and in the β-position of the vinyl group, which are obtained from γ-piperidinones via 4-ethynyl-4-piperidinols[332] or 4-vinylethynyl-4-piperidinols[333], are converted into substituted perhydro-1,7-naphthyridines on reacting with primary amines:

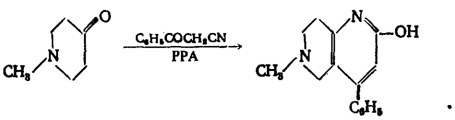


The same divinyl ketones have been used in the syntheses of piperidine–thiopyran (reaction with hydrogen sulphide) and piperidine–pyran (reaction with water) condensed systems[334,335].

Catalytic hydrogenation of 5-(β-cyanoethyl)-1,2,5-trimethyl-4-piperidinone led to the isolation of 4*a*,6,7-trimethyldecahydro[1,6]naphthyridine[92]:

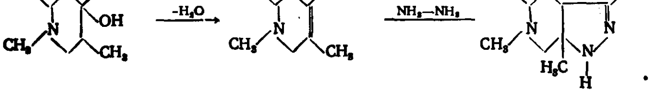


The condensation of 1-methyl-4-piperidinone with benzoylacetonitrile in the presence of polyphosphoric acid (PPA) led to the formation of 2-hydroxy-6-methyl-4-phenyl-5,6,7,8-tetrahydro[1,6]naphthyridine[336]:

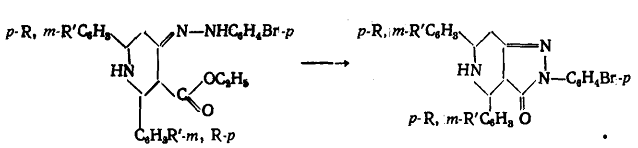


The Synthesis of the Condensed System Comprising Piperidine and Pyrazole

When the product of the dehydration of 4-ethynyl-1,2,5-trimethyl-4-piperidinol reacts with hydrazine hydrate, 2*a*,4,5,7-tetramethyl-2*a*,3,4,5,6,6*a*-hexahydropyrazolino[5,4-*c*]pyridine is formed[337]:

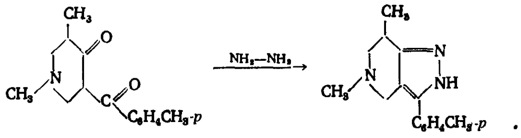


The intramolecular condensation of the *p*-bromophenylhydrazone of 3-ethoxycarbonyl-2,6-di-(*m*-methoxy-*p*-hydroxyphenyl)-4-piperidinone results in the formation of the corresponding 2,4,6-triaryl-3-oxo-3,3*a*,4,5,6,7-hexahydropyrazolo[4,3-*c*]pyridine[338]:

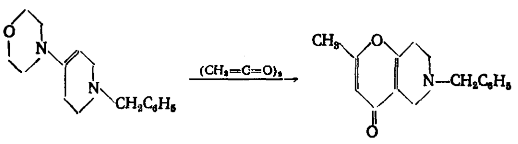


The syntheses of analogous condensed systems have also been described[339,340].

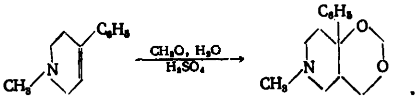
5,7-Dimethyl-3-*p*-tolyl-4,5,6,7-tetrahydropyrazolo[4,3-*c*]pyridine has been obtained by the reaction of 1,3-dimethyl-5-*p*-methylbenzoyl-4-piperidinone with hydrazine[341]:



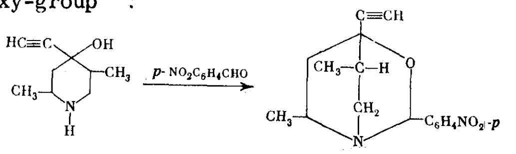
The analogous tetrahydropyrazolopyridine has been synthesised by condensing 1-acetyl-3-ethoxycarbonyl-4-piperidinone with phenylhydrazine[307]. 1-Benzoyl-4-morpholino-1,2,3,6-tetrahydropyridine (an enamine obtained from 1-benzyl-4-piperidinone) condensed with diketen to form 6-benzyl-2-methyl-5,6,7,8-tetrahydro-6-azochromone[342]:



6-Methyl-8*a*-phenyl-4*a*,5,6,7,8,8*a*-hexahydropyrido[4,5*α*]-1,3-dioxan has been synthesised by the Prins reaction from the product of the dehydration of 1-methyl-4-phenyl-4-piperidinol (obtained from 1-methyl-4-piperidinone)[343]:

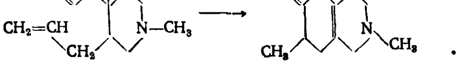


6-Ethynyl-4,7-dimethyl-2-*p*-nitrophenyl-1-oxa-3-azabicyclo[2,2,2]octane has been obtained from the γ-isomer of 4-ethynyl-2,5-dimethyl-4-piperidinol (with an axial hydroxy-group)[344]:

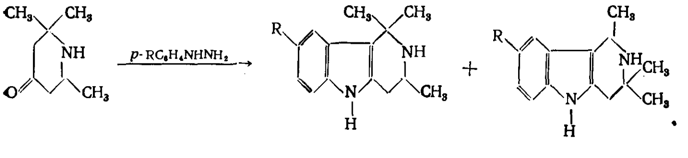


Synthesis of Tricyclic Heterocycles

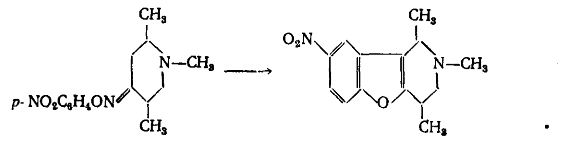
3-Allyl-1-methyl-4-phenyl-4-piperidinol, obtained from the corresponding γ-piperidinone, is converted on heating with 20% hydrochloric acid into 2,9-dimethyl-1,2,3,4,9,10-hexahydro-2-azaphenanthrene[100]:



The Fischer cyclisation of the arylhydrazones of certain γ-piperidinones has been investigated. In particular, the formation of 2,4,4-trimethyl-1,2,3,4-tetrahydro-γ-carboline and its isomer as regards the positions of the substituents in the nitrogen-containing six-membered ring has been demonstrated using the arylhydrazone of 2,2,6-trimethyl-4-piperidinone as an example. Analogous syntheses have also been described[345]:

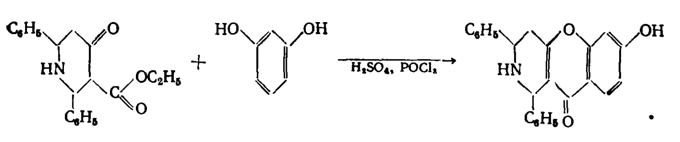


The cyclisation of the *p*-nitrophenylether of the oxime of 1,2,5-trimethyl-4-piperidinone to give 1,2,4-trimethyl-8-nitro-1,2,3,4-tetrahydrobenzofuro[3,2-*c*] pyridine has been achieved[346]:



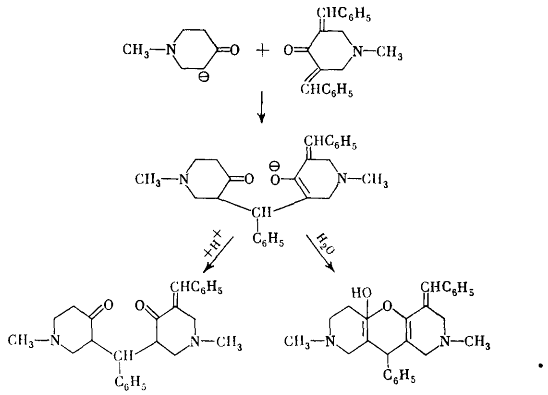
The condensation of *o*(*p*)-nitrophenyl ethers of the oximes of 1,3-dialkyl-4-piperidinones in ethanol in the presence of hydrogen chloride yielded 2,4-dialkyl-4*a*-ethoxy-1,2,3,4,4*a*,9*b*-hexahydro-6(8)-nitrobenzofuro[3,2-*c*]pyridine[347].

The condensed system comprising a partly hydrogenated pyridine and benzopyran has been obtained by the reaction of 3-ethoxycarbonyl-2,6-diphenyl-4-piperidinone with resorcinol[348]:

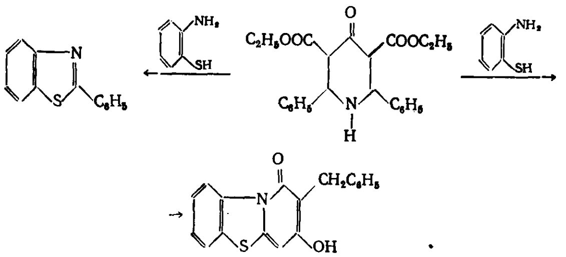


5-Oxo-1,2,3,4-tetrahydro-5*H*-[1]benzopyrano[3,4-*c*]-pyridines, substituted similarly in the dehydropiperidine and benzene rings, have been described in patents[349,350].

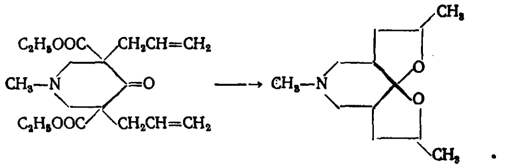
A complex mixture of substances is formed when γ-piperidinones interact with aromatic aldehydes in the presence of bases. When 1-methyl-4-piperidinone condenses with benzaldehyde, 3-benzylidene-5-[α-(1-methyl-4-oxo-3-piperidyl)benzyl]-1-methyl-4-piperidinone and 4-benzylidene-10*a*-hydroxy-2,7-dimethyl-9-phenyl-10-oxa-2,7-diaza-9*H*-1,2,3,4,5,6,7,8,8*a*,10*a*-decahydroanthracene are formed in addition to 3,5-dibenzylidene-1-methyl-4-piperidinone[80]. It has been suggested that there is initial Michael addition of the piperidinone anion to 3,5-dibenzylidene-1-methyl-4-piperidinone, whereupon the resulting enolate anion is converted in two steps into the above heterocyclic compounds[351,352]:



The reaction of *o*-aminothiophenol with 3,5-diethoxycarbonyl-2,6-diphenyl-4-piperidinone in boiling xylene led to the isolation of 2-phenylbenzothiazole and 2-benzyl-3-hydroxy-1-oxo-1*H*-benzo[*d*]pyrido[2,1-*b*]thiazole[353]. Their formation involves the cleavage of the piperidine ring, the mechanism of which has not so far been elucidated:

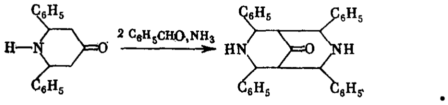


Hydrolysis of the diethyl ester of 3,5-diallyl-1-methyl-4-oxopiperidine-3,5-dicarboxylic acid followed by its decarboxylation is accompanied by the hydration of the allyl groups and the formation of the acetal derivative of 1,5′,5″-trimethylbis(tetrahydrofurano)-3′,2′ : 3,4 ; 2″,3″ : 4,5-piperidine[354]:

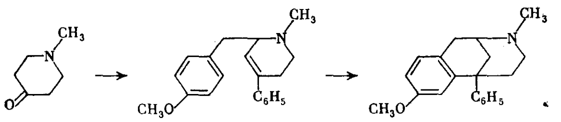


Synthesis of Bispidines

9-Oxo-2,4,6,8-tetraphenylbispidine is formed from 2,6-diphenyl-4-piperidinone, benzaldehyde, and ammonia[355]. Bispidines have also been synthesised by the condensation of γ-piperidinones with formaldehyde and methylamine[356,357]:



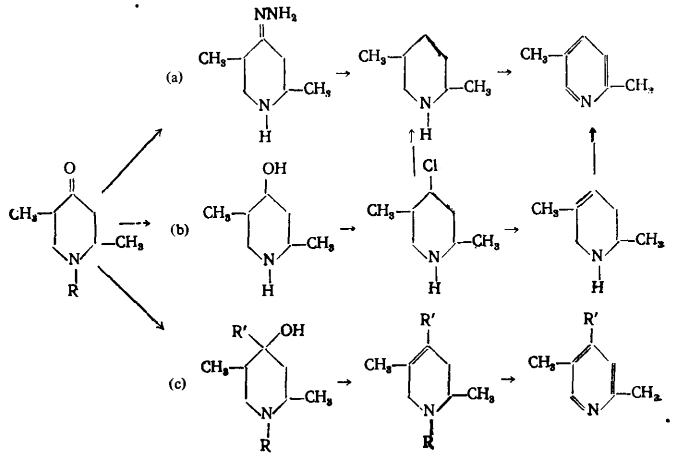
2-*p*-Methoxybenzyl-1-methyl-4-phenyl-1,2,3,6-tetrahydropyridine was obtained by a series of successive transformations (phenyl-lithium synthesis, dehydration, formation of a salt with *p*-methoxybenzyl chloride, and its intramolecular Stevens rearrangement) from 1-methyl-4-piperidinone and was then converted by the Graebe method into a substituted benzomorphan[358]:



An analogous synthesis has been achieved starting from 1,3-dimethyl-4-piperidinone[359]. After treating 2-benzyl-1-methyl-4-piperidinone with 48% hydrobromic acid, 5-hydroxy-2-methyl-6,7-benzomorphan was isolated[360].

The ease of formation of γ-piperidinones substituted in a wide variety of ways makes it possible to employ them for the synthesis of pyridine bases. It has been shown for 2,6-diphenyl-4-piperidinol that, when it is treated with sulphur *in vacuo* up to 200°C, 2,6-diphenylpyridine is formed in approximately 90% yield[19]. It has been reported that tertiary γ-piperidinols are converted into pyridine bases on heating to 220–240°C with 20 wt.% of a palladium catalyst[134]. Pyriding has been obtained in a yield exceeding 90% on dehydrogenating piperidine (5% Pd, 300–400°C)[361]. A method has been developed for the dehydrogenation of piperidine bases to pyridine bases with the aid of a pyridine N-oxide[362].

In order to obtain pyridine bases from γ-piperidones, the following procedures are used: (a) reduction of γ-piperidinones by the Wolff–Kishner method to substituted piperidines with subsequent dehydrogenation in the presence of industrial K-12 and K-16 type catalysts[363]; (b) reduction of γ-piperidinones to γ-piperidinols, the replacement of the hydroxy-group in the latter by a halogen and then of the halogen by hydrogen, and dehydrogenation (or dehydrochlorination), dehydrogenation being the last stage; the yield in the dehydrogenation stage is more than 90%;[23,24,363]: (c) the conversion of γ-piperidinones into secondary and also tertiary piperidinols and their dehydration followed by the dehydrogenation and *N*-dealkylation of the resulting tetrahydropyridines[144–146, 202,203,364–368]:

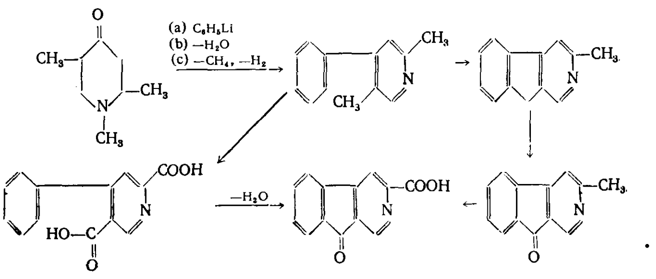


More than 150 individual pyridine bases with different structures have been obtained by means of these synthetic procedures from 1,2,5-trimethyl-4-piperidinone alone[34, 144–146,156–158,202,237,269,363–366,369–389].

γ-Piperidinones have become important starting materials in the syntheses of individual and substituted pyridine bases having specified structures. The study of the hydrogenation of 4-aryl- and 4-alkylaryl-pyridines obtained in this way established that, in the presence of catalysts such as rhenium heptasulphide, platinum sulphide, and palladium sulphide, only the pyridine ring undergoes selective hydrogenation, 4-aryl- and 4-alkylaryl-piperidines being formed in yields up to 99, 93, and 40% respectively. If the hydrogenation is carried out in alcohol, *N*-alkylation takes place simultaneously[390–393].

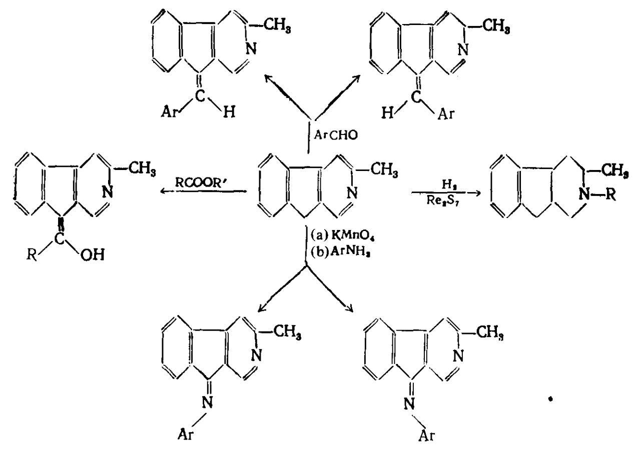
A characteristic feature of the structure of many pyridine bases obtained from 1,2,5-trimethyl-4-piperidinone is that the β-position contains a methyl group and the γ-position an aryl or alkylaryl group. These features have been used to synthesise condensed polycyclic nitrogen-containing heterocyclic compounds from such pyridine bases by dehydrocyclisation at 500–560°C in the presence of K-12 and K-16 catalysts.

2-Azafluorenes are formed from 4-aryl-3-methylpyridines, while 2,4-diaryl-3-methylpyridine gives rise to 2-aza and 4-aza-fluorenes[394]. An example of such syntheses is proved by the preparation of 3-methyl-2-azafluorenone and 9-oxo-2-azafluorene-3-carboxylic acid[373,395]. 9-Oxo-2-azafluorene-4-carboxylic acid was obtained similarly[203]:

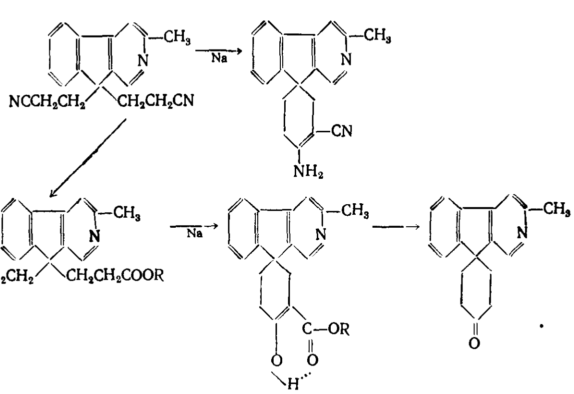


4-Aryl-2,5-dimethylpyridines with different alkyl substituents in the benzene ring have also been used to synthesise 2-azafluorenes[168,374]. The dehydrocyclisation of 3-methyl-2,4,6-triphenylpyridine (obtained from 1,3-dimethyl-2,6-diphenyl-4-piperidinone) leads to the formation of 1,3-diphenyl-2-azafluorene and 1,3-diphenyl-4-azafluorene. The former has also been obtained in the dehydrocyclisation of 2,6-diphenyl-4-*o*-tolylpyridine[176]. 3-Methyl-2-azafluorenone has been used in the syntheses of many 9-aryl(alkylaryl)-3-methyl-2-azafluorenols and their esters[396]. The geometrical isomers of 9-arylidene derivatives of 2-azafluorene and 3-methyl-2-azafluorene have been obtained in a study of their condensation with aromatic aldehydes, and it has been established that they are readily interconverted[397]. *N*-(3-Methyl-2-aza-9-fluorenylidene)arylamines, formed on condensation of 3-methyl-2-azafluorenone with aromatic amines, exist in the form of an equilibrium mixture of the *cis*- and *trans*-isomers (^{1}H NMR data)[398]. The enolic form is the stable structure of 9-acyl(aroyl) derivatives of 2-azafluorenes, its stabilisation being due to the interaction of the acid enolic hydrogen with the nitrogen of the pyridine ring[399,400]. When 3-methyl-2-azafluorene was reduced with sodium in alcohol, two isomers of 2-methyl-5*H*-indano[2,1-*c*]-piperidine were isolated[401] and their structures were subsequently examined[402,403]. It has been shown in a number of instances that the hydrogenation of substituted 2-azafluorenes in the presence of rhenium heptasulphide is selective, only the pyridine ring being hydrogenated with simultaneous reduction of the oxo- and hydroxy-groups in the 9-position and alkylation at the nitrogen atom when the hydrogenation is carried out in alcohol.

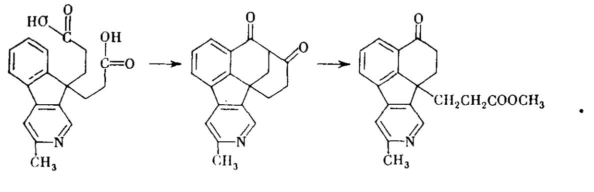
Two isomers of the indanopiperidine were also obtained in this instance[404,405].



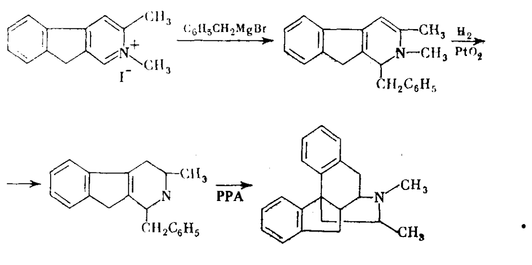
A new heterocyclic system—4'-amino-3'-cyano-3-methylspiro[2-azafluorene-9,1'-cyclohex-3'-ene]—has been obtained by the Dieckmann condensation from 9,9-di-(β-cyanoethyl)-3-methyl-2-azafluorene (synthesised by the Michael reaction from 3-methyl-2-azafluorene), while the condensation of 9,9-di-(β-ethoxycarbonylethyl)-3-methyl-2-azafluorene gave 3'-alkoxycarbonyl-4'-hydroxy-3-methylspiro[2-azafluorene-9,1'-cyclohex-3'-ene], which was subsequently converted into a spiroketone[406]. Analogous spirostructures have been obtained by the reaction of 3-methyl-2-azafluorene with αβ-unsaturated acid esters in the presence of sodium:



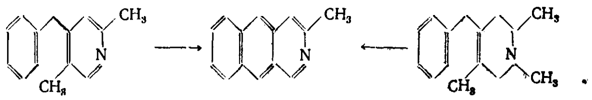
A new heterocyclic system—9-methyl-4,13-dioxo-8-aza-4,5,6,6*a*-tetrahydro-5,6*a*-propanofluoranthene—has been obtained by the cyclodehydration of 9,9-di-(β-carboxyethyl)-3-methyl-2-azafluorene under the influence of polyphosphoric acid. 6*a*-(2-Methoxycarbonylethyl)-9-methyl-4-oxo-8-aza-4,5,6,6*a*-tetrahydrofluoranthene is formed from this compound on treatment with methanol and sulphuric acid[407]:



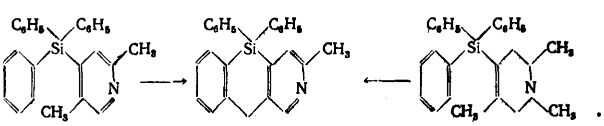
An analogue of morphinan—2,3-dimethyl-6,7-benzo-5,9-(1',2'-indano)-2-azabicyclo[3,3,1]non-6-ene—has been obtained from the methiodide of 3-methyl-2-azafluorene by a series of consecutive transformations[408]:



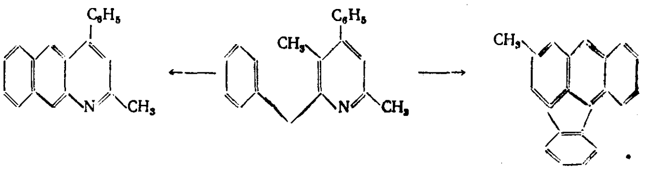
4-(2,5-Dimethyl)pyridines have been used to synthesise many benzo[*g*]isoquinolines, which have been little investigated. The same method (catalytic dehydrocyclisation) was used[383,385,396,409]:



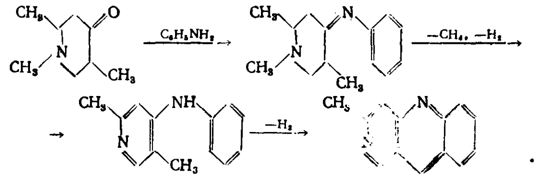
2,5-Dimethyl-4-triphenylsilylpyridine (it was synthesised from 1,3,6-trimethyl-4-triphenylsilyl-1,2,3,6-tetrahydropyridine) also undergoes dehydrocyclisation with formation of 2-methyl-9,9-diphenyl-9,10-dihydro-9-sila-3-aza-anthracene[410]:



The benzo[*g*]quinoline structure is formed on dehydrocyclisation of 2,5-dimethyl-4-phenyl-6-benzylpyridine, the products being 2-methyl-3-azabenzo[*f*]fluoranthene together with 2-methyl-4-phenylbenzo[*g*]quinoline[387]:

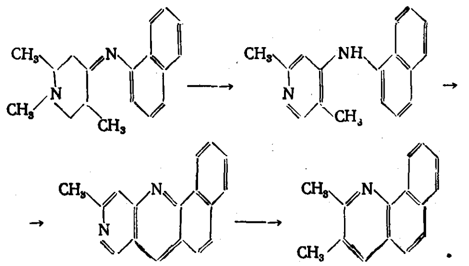


Yet another application of γ-piperidinones in the syntheses of heterocyclic compounds has been developed—the preparation from the latter of Schiff bases[41] and their catalytic transformations. It has been established[369] that *N*-(1,2,5-trimethyl-4-piperidylidene)aniline (obtained from 1,2,5-trimethyl-4-piperidinone and aniline) is converted in the presence of the K-12 catalyst at 470°C into (2,5-dimethyl-4-pyridyl)phenylamine, from which 7-methyl-2,3-benzo-1,6-naphthyridine is formed in the presence of the same catalyst[395]. The Schiff base obtained from 4-amino-1,2,5-trimethylpiperidine and benzaldehyde is converted into αβ'-lutidine at 400°C:[377]



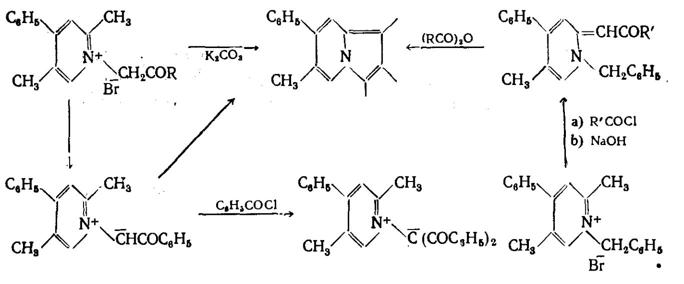
The reactions under analogous conditions of the Schiff bases obtained from 1,2,5-trimethyl-4-piperidinone and naphthylamines take place in a more complex manner.

N-(2,5-Dimethyl-4-pyridyl)-α-naphthylamine, 9-methylnaphtho[1,2-*b*][1,6]naphthyridine, and 2,3-dimethyl-4-azaphenanthrene have been obtained from *N*-(1,2,5-trimethyl-4-piperidylidene)-α-naphthylamine. The last Schiff base is apparently formed as a result of the degradation of naphthonaphthyridine[411]:

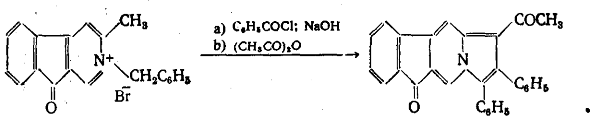


The following compounds were isolated after the analogous reactions of *N*-(1,2,5-trimethyl-4-piperidylidene)-β-naphthylamine: *N*-(2,5-dimethyl-4-pyridyl)-β-naphthylamine, 9-methylnaphtho[2,1-*b*][1,6]naphthyridine, and 2,3-dimethyl-1-azaphenanthrene[412].

The availability of substituted pyridine bases obtained from γ-piperidinones made it possible to expand the research into indolizine systems. Indolizines have been obtained directly from the quaternary *N*-β-oxoalkylpyridinium salts, from 1-benzyl-5-methyl-4-phenyl-3-phenacylidene-1,2-dihydropyridine, and from pyridine ylides. The stable dibenzoylmethylides were isolated in the study of the last group of compounds[368,413–415]:



A condensed system comprising indene and indolizine, namely 1-acetyl-5-oxo-2,3-diphenyl-5*H*-indeno[2,1-*f*]-indolizine, and other analogues have been synthesised[413,414]:



It follows from the present review that γ-piperidinones play an appreciable rôle in the development of the chemistry of piperidine and certain other heterocyclic compounds. The synthetic possibilities of γ-piperidinones in this respect have apparently been by no means exhausted.

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The Methods of Synthesis and Properties of Conjugated Enallenic Hydrocarbons

I.Z.Egenburg

The methods of synthesis of conjugated enallenic hydrocarbons are surveyed and their physical and chemical properties are discussed.

The bibliography includes 90 references.

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I. INTRODUCTION

Enallenic hydrocarbons containing the allene group conjugated with a double bond were obtained for the first time (with a rigorous demonstration of their structure) in 1958. The information available at the present time concerning the methods of synthesis and the chemical behaviour of these compounds is limited. However, the available data show that conjugated enallenes are interesting objects of study. The unusual stereochemistry of the allene group, which is particularly clearly manifested in enallenes, determines the ability of only one double bond of this group to participate in conjugation with the α-ethylenic bond, which is the reason for the unusual physical and chemical properties of these hydrocarbons. The likely usefulness of conjugated enallenic hydrocarbons in experimental organic chemistry has been demonstrated by their synthesis from aromatic and methylenecyclohexene compounds, which are relatively difficult to obtain, conjugated cyclopentenones, methylenecyclobutene derivatives, allenic alcohols, epoxides, etc. It has been established that the enallenic conjugated system of bonds occurs in certain natural antibiotics, attractants, and the pigments of algae, sea urchins, and the flowers and leaves of many plants. Allenic compounds with an α-ethylenic bond are also produced by many species of fungi. Since some of these compounds exhibit distinct antimicrobial and fungicidal activities, the study of the structure and biogenesis of natural enallenic derivatives is an important practical task.

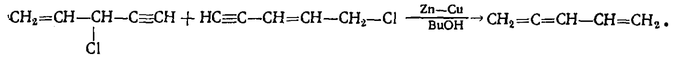
The development of the chemistry of enallenic hydrocarbons is mainly due to the development of two fundamental preparative methods for their synthesis: the method of Petrov and Kormer and Bertrand's method. It is to be expected that further research in the chemistry of conjugated enallenic hydrocarbons will lead to the development of new methods of their synthesis and to extensive practical applications of these hydrocarbons.

II. METHODS OF SYNTHESIS

1. THE ANIONOTROPIC REARRANGEMENT OF ENYNE AND PROPARGYL SYSTEMS

(a) The Reduction of Halogenoenynes by Metals

Penta-1,2,4-triene (I), the parent compound of the class of conjugated enallenic hydrocarbons, was obtained for the first time by analogy with Ginzburg's method[1], on treating a mixture of the chloropentenynes (II) and (III)—derivatives of pent-1-en-4-yn-3-ol[2]—with the zinc–copper couple in butanol; the enallene (I) with 94% purity was isolated in 75% yield[3].

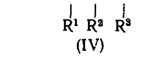


$$CH_2{=}CH{-}\underset{Cl}{CH}{-}C{\equiv}CH + HC{\equiv}C{-}CH{=}CH{-}CH_2{-}Cl \xrightarrow[BuOH]{Zn-Cu} CH_2{=}C{=}CH{-}CH{=}CH_2 .$$

(II) (III) (I)

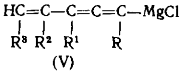
The use of the *trans*-isomer of the chloropentenyne (III) under these conditions made it possible to obtain compound (I) with 97% purity and in 70% yield.

During the reduction of chloroenynes with the zinc–copper couple, accompanied by the anionotropic rearrangement, an organozinc compound is apparently formed as an intermediate[4]. This is confirmed by the experimental observation of the formation of organomagnesium compounds in the reactions of analogues of the chloropentenyne (III) with magnesium. It has been shown[5,6] that the substituted chloropentenynes (IV) react with magnesium in ether at a low temperature to form the derivatives (V), which have the enallenic structure:



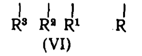
$$RC{\equiv}C{-}\underset{R^1}{C}{=}\underset{R^2}{C}{-}\underset{R^3}{C}HCl$$

(IV)



$$\underset{R^3}{HC}{=}\underset{R^2}{C}{-}\underset{R^1}{C}{=}C{=}\underset{R}{C}{-}MgCl$$

(V)

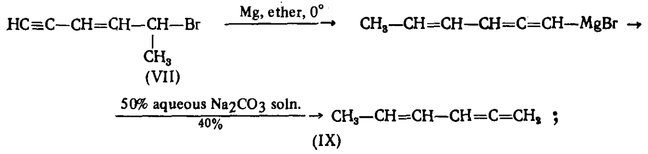


$$\underset{R^3}{HC}{=}\underset{R^2}{C}{-}\underset{R^1}{C}{=}C{=}\underset{R}{CH}$$

(VI)

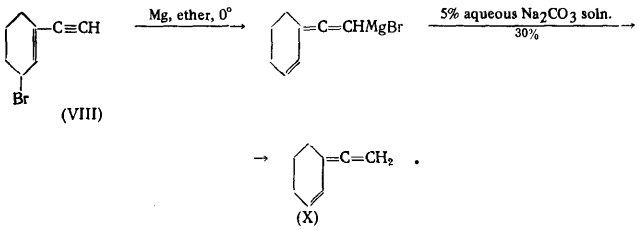
(a) $R{=}R^1{=}R^2{=}R^3{=}H$; (b) $R{=}R^2{=}R^3{=}H$, $R^1{=}CH_3$; (c) $R{=}R^3{=}H$, $R^1{=}R^2{=}CH_3$; (d) $R{=}R^1{=}R^2{=}H$, $R^3{=}CH_3$; (e) $R{=}CH_3$, $R^1{=}R^2{=}R^3{=}H$; (f) $R{=}H$, $R^1{=}R^2{=}R^3{=}CH_3$; (g) $R{=}H$, $R^1+R^2{=}$tetramethylene, $R^3{=}CH_3$; (h) $R{=}H$, $R^1{=}CH_3$, $R^2+R^3{=}$tetramethylene.

This discovery made it possible to use the above reaction to synthesise conjugated enallenic hydrocarbons. Thus the primary chloro-derivatives (IV, a–c, e) are converted, on treatment with magnesium and subsequent hydrolysis of the resulting organomagnesium compounds (V), into the corresponding enallenes (VI, a–c, e) in a satisfactory yield (31–55%).[5,6] The secondary chloroenynes (IV, d, f–h) do not react with magnesium either in boiling ether or in tetrahydrofuran (THF). However, the corresponding bromo-derivatives readily form organomagnesium compounds in the cold in ether, which has been demonstrated by the synthesis of the enallenic hydrocarbons (IX) and (X) from the bromo-derivatives (VII) and (VIII):



$$HC{\equiv}C{-}CH{=}CH{-}\underset{\underset{CH_3}{|}}{CH}{-}Br \xrightarrow{\text{Mg, ether, }0^\circ} CH_3{-}CH{=}CH{-}CH{=}C{=}CH{-}MgBr \rightarrow \xrightarrow[40\%]{50\%\text{ aqueous }Na_2CO_3\text{ soln.}} CH_3{-}CH{=}CH{-}CH{=}C{=}CH_2\ ;$$

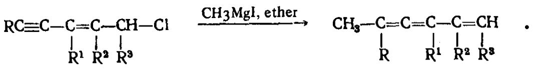
(VII) (IX)



(VIII) (X)

(b) The Interaction of Propargyl Halides, Halogenoenynes, and Ethers with Grignard Reagents

The chloropentenynes (IV, a–h) are converted into conjugated enallenes (XI) in 20–80% yield on treatment with methylmagnesium iodide in boiling† ether over a period of 2–3 h:[6,7]



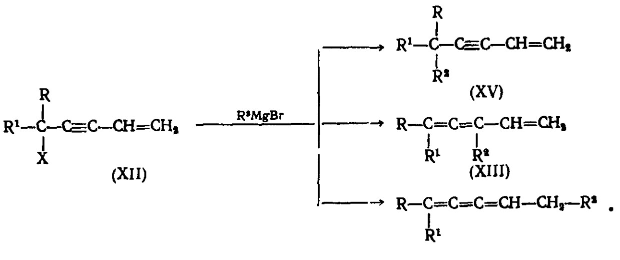
$$R C{\equiv}C{-}\underset{\underset{R^1}{|}}{C}{=}\underset{\underset{R^2}{|}}{C}{-}\underset{\underset{R^3}{|}}{CH}{-}Cl \xrightarrow{CH_3MgI,\text{ ether}} CH_3{-}\underset{\underset{R}{|}}{C}{=}C{=}\underset{\underset{R^1}{|}}{C}{-}\underset{\underset{R^2}{|}}{C}{=}\underset{\underset{R^3}{|}}{CH}\ .$$

(IV, a–h) (XI)

The enallenes (XI) were isolated from the reaction mixture by chromatographic methods. The above treatment of the chloroenyne (IV, f) gave a direct substitution product as the main reaction product. It has been established[6] that conjugated enallenes cannot be obtained from the chloroenynes (IV, a–h) using other Grignard reagents.

Comparison of the above two methods of synthesis of enallenes using chloropentenynes of type (IV) leads to the conclusion that the second method is preferable on the preparative scale, since it makes it possible to obtain the desired products with a higher purity and in higher yields. Furthermore, it permits the use of both primary and secondary chloroenynes.

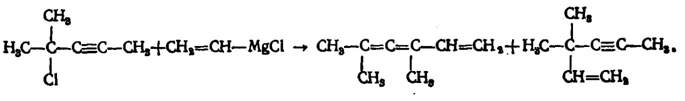
It has been shown[8] that the tertiary chlorides (XII, X = Cl) react with the Grignard reagent to form a mixture of enallenic and cumulenic hydrocarbons [compounds (XIII) and (XIV)], which are obtained from the initial compound as a result of a substitution reaction and the acetylene–allene–cumulene rearrangement. The reaction product contains a certain amount of the enyne hydrocarbon (XV) as a result of the "normal" substitution of chlorine in compound (XII)



$$R^1{-}\overset{\overset{R}{|}}{\underset{\underset{X}{|}}{C}}{-}C{\equiv}C{-}CH{=}CH_2 \xrightarrow{R^2MgBr} \begin{cases} R^1{-}\overset{\overset{R}{|}}{\underset{\underset{R^2}{|}}{C}}{-}C{\equiv}C{-}CH{=}CH_2 & \text{(XV)} \\ R{-}\underset{\underset{R^1}{|}}{C}{=}C{=}\underset{\underset{R^2}{|}}{C}{-}CH{=}CH_2 & \text{(XIII)} \\ R{-}\underset{\underset{R^1}{|}}{C}{=}C{=}C{=}CH{-}CH_2{-}R^2\ . & \text{(XIV)} \end{cases}$$

(XII)

The enyne (XV) is absent from the reaction mixture obtained by the analogous treatment of the ethers (XII, X = OAlk) and containing only compounds (XIII) and (XIV).[9] The overall yield and composition of the hydrocarbon mixture formed in the above reaction for different X, R, R^1, and R^2 are presented in Table 1. The reaction of vinylmagnesium chloride and 4-chloro-4-methylpent-2-yne (XVI) yields a mixture of the conjugated enallene (XVII) and the enyne (XVIII):[10]



$$H_3C{-}\overset{\overset{CH_3}{|}}{\underset{\underset{Cl}{|}}{C}}{-}C{\equiv}C{-}CH_3 + CH_2{=}CH{-}MgCl \rightarrow CH_3{-}\underset{\underset{CH_3}{|}}{C}{=}C{=}\underset{\underset{CH_3}{|}}{C}{-}CH{=}CH_2 + H_3C{-}\overset{\overset{CH_3}{|}}{\underset{\underset{CH{=}CH_2}{|}}{C}}{-}C{\equiv}C{-}CH_3 .$$

(XVI) (XVII) (XVIII)

Vinylmagnesium bromide and propargyl bromide react to form a 2·3 mixture of pent-1-en-4-yne (XIX) and penta-1,2,4-triene (I):[11]

$$HC{\equiv}C{-}CH_2{-}Br + CH_2{=}CH{-}MgBr \rightarrow \underset{\text{(XIX)}}{HC{\equiv}C{-}CH_2{-}CH{=}CH_2} + \underset{\text{(I)}}{CH_2{=}C{=}CH{-}CH{=}CH_2}\ .$$

Subsequent Bertrand isomerisation[12] of the mixture of hydrocarbons (XIX) and (I) on treatment with NaOH in methanol give the pure enallene (I). The latter can also be isolated by removing the enyne (XIX) from the reaction mixture on treatment with an alcoholic solution of silver nitrate.

Table 1. The overall yields and compositions of the hydrocarbon mixtures obtained in the reactions of the enynes (XII) with Grignard reagents[9].

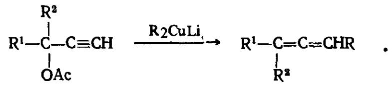
Enyne derivative (XII)			R^2MgBr	Content in reaction mixture, %			Overall yield of (XIII) + (XIV) + (XV), %
R	R_1	X	R^2	(XIII)	(XIV)	(XV)	
CH_3	CH_3	Cl	C_2H_5	61	35	4	57
CH_3	n-C_4H_9	Cl	C_2H_5	57	48	5	77
C_2H_5	n-C_4H_9	Cl	C_2H_5	46	38	6	77
CH_3	CH_3	Cl	C_6H_5	54	36	10	46
CH_3	CH_3	CH_3O	C_2H_5	86	14	0	62
CH_3	CH_3	CH_3O	n-C_3H_7	86	14	0	51
CH_3	CH_3	CH_3O	n-C_4H_9	81	19	0	49
CH_3	CH_3	CH_3O	iso-C_3H_7	0	100	0	44
CH_3	CH_3	CH_3O	iso-C_4H_9	0	100	0	40
CH_3	CH_3	CH_3O	t-C_4H_9	0	100	0	40
CH_3	CH_3	C_2H_5O	C_2H_5	77	23	0	66
CH_3	CH_3	n-C_3H_7O	C_2H_5	82	18	0	61
CH_3	CH_3	n-C_4H_9O	C_2H_5	66	34	0	49
CH_3	CH_3	iso-C_3H_7O	C_2H_5	54	46	0	45
CH_3	CH_3	iso-C_4H_9O	C_2H_5	30	70	0	38

---

† Certain chlorides react at room temperature.

(c) Reduction of Enynyl Acetates with Dialkyl-lithium Cuprates

On treatment with dialkyl-lithium cuprates, propargyl acetates give high yields of alkylallenes[13]:



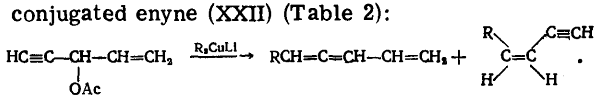
$$R^1{-}\overset{\displaystyle R^2}{\underset{\displaystyle OAc}{C}}{-}C{\equiv}CH \xrightarrow{R_2CuLi} R^1{-}\underset{\displaystyle R^2}{C}{=}C{=}CHR \;.$$

It has been shown[14] that this reaction can also be extended to the synthesis of conjugated enallenes when acetates having the enyne structures are used as the starting compounds.

Table 2. The compositions of the hydrocarbon mixtures obtained on treating the enynyl acetate (XX) with dialkyl-lithium cuprates R_2CuLi.[14]

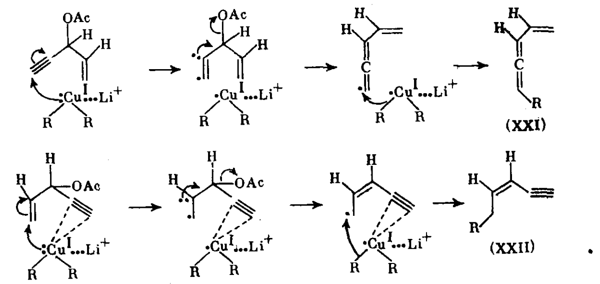
R	Content in reaction mixture, %		Overall yield of (XXI) + (XXII), %
	(XXI)	(XXII)	
CH_3	94	6	42
C_4H_9	80	20	60
C_8H_{17}	90	10	52

Thus the reaction of 3-acetylpent-1-en-4-yne (XX) with R_2CuLi in ether (between −20° and −30°C) results in the formation of the conjugated enallene (XXI) together with the conjugated enyne (XXII) (Table 2):



(XX) (XXI) (XXII)

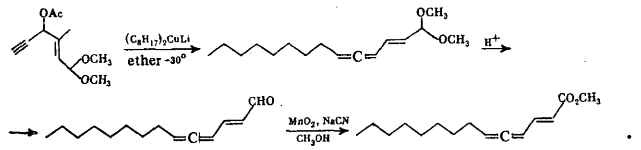
It follows from the data in Table 2 that the main reaction product is the enallenic hydrocarbon (XXI), the formation of which is believed[14] to be the result of the addition of dialkyl-lithium cuprate to the triple bond of the initial acetate (XX), while the enyne (XXII) results from the addition of the cuprate to the double bond:



(XXI)

(XXII)

The ester (XXIII), which is an insect attractant and is therefore of considerable interest, has been synthesised by this method[14]:



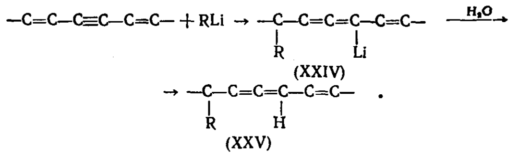
(XXIII)

2. REACTIONS INVOLVING 1,4-ADDITION TO ENYNE AND DIENYNE SYSTEMS

(a) The Addition of Organolithium, Organocalcium, and Organobarium Compounds to Conjugated Dienyne Hydrocarbons

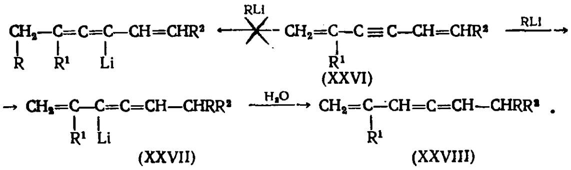
Petrov and Kormer developed a widely used preparative method of synthesising enallenes by treating conjugated dienyne hydrocarbons with alkyl-lithium in ether at a low temperature[15-19]. The following facts were established.

(1) The RLi reagent adds in the 1,4-positions of the enyne fragment of the conjugated dienyne system with formation of the lithium-containing adduct (XXIV) whose hydrolysis yields the enallene (XXV):



$$-C{=}C{-}C{\equiv}C{-}C{=}C- + RLi \rightarrow -\underset{\displaystyle R}{C}{-}C{=}C{=}\underset{\displaystyle Li}{C}{-}C{=}C- \;\xrightarrow{H_2O}$$
$$\text{(XXIV)}$$
$$\rightarrow -\underset{\displaystyle R}{C}{-}C{=}C{=}\underset{\displaystyle H}{C}{-}C{=}C- \;.$$
$$\text{(XXV)}$$

(2) The alkyl-lithium undergoes 1,4-addition, leading to the formation of an allenic system, only to the enyne fragments containing an unsubstituted vinyl group. Thus the dienyne (XXVI, $R^1 = CH_3$, $R^2 = H$) reacts with alkyl-lithium to form exclusively the lithio-derivative (XXVII)—the product of the addition of alkyllithium to the "vinylacetylene" fragment and not the "isopropenylacetylene" fragment of the dienyne system, as a result of which the enallenic hydrocarbon (XXVIII) is the sole product of the above reaction[16]:

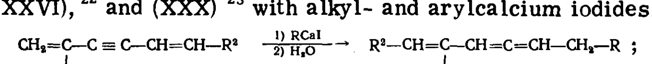


$$\underset{\displaystyle R}{CH_2}{-}\underset{\displaystyle R^1}{C}{=}C{=}\underset{\displaystyle Li}{C}{-}CH{=}CHR^2 \;\overset{RLi}{\nleftarrow}\; CH_2{=}\underset{\displaystyle R^1}{C}{-}C{\equiv}C{-}CH{=}CHR^2 \xrightarrow{RLi}$$
$$\text{(XXVI)}$$
$$\rightarrow CH_2{=}\underset{\displaystyle R^1}{C}{-}\underset{\displaystyle Li}{C}{=}C{=}CH{-}CHRR^2 \xrightarrow{H_2O} CH_2{=}\underset{\displaystyle R^1}{C}{-}CH{=}C{=}CH{-}CHRR^2 \;.$$
$$\text{(XXVII)} \qquad \text{(XXVIII)}$$

(3) The alkyl group of the reagent always adds to the terminal atom of the unsubstituted vinyl group.

The above characteristics of the addition of organolithium reagents to conjugated dienyne hydrocarbons can be accounted for by a coordination reaction mechanism[19]. The same characteristics hold also[20] in the reaction of aryl- and naphthyl-lithium with the dienyne hydrocarbon (XXVI, $R^1 = CH_3$, $R^2 = H$). Because of this, the enallenic hydrocarbon (XXVIII, $R = C_6H_5$, $2\text{-}CH_3C_6H_4$, $3\text{-}CH_3C_6H_4$, or α-naphthyl) is the only product of the above reaction.

Conjugated enallenic hydrocarbons can also be obtained by the reactions of the dienyne hydrocarbons (XXIX),[21] (XXVI),[22] and (XXX)[23] with alkyl- and arylcalcium iodides:



$$CH_2{=}\underset{\displaystyle R^1}{C}{-}C{\equiv}C{-}CH{=}CH{-}R^2 \xrightarrow[2)\,H_2O]{1)\,RCaI} R^2{-}CH{=}\underset{\displaystyle R^1}{C}{-}CH{=}C{=}CH{-}CH_2{-}R \;;$$

(XXIX): $R^1{=}H$, $R^2{=}H$; $R{=}C_2H_5$, $n\text{-}C_3H_7$, $n\text{-}C_4H_9$, $iso\text{-}C_4H_9$, $n\text{-}C_5H_{11}$;

(XXVI): $R^1{=}CH_3$, $R^2{=}H$; $R{=}C_2H_5$, $n\text{-}C_3H_7$, $n\text{-}C_4H_9$, $iso\text{-}C_4H_9$, $n\text{-}C_5H_{11}$, C_6H_5, $CH_3C_6H_4$;

(XXX): $R^1 = H$, $R^2 = CH_3$; $R = C_2H_5$, $n\text{-}C_3H_7$, $n\text{-}C_4H_9$.

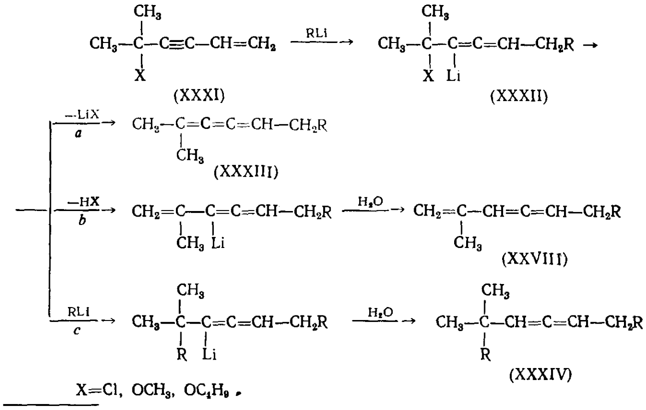
The above process, which takes place at room temperature over a period of several minutes, is, however, complicated by a competing reaction of the Wurtz type. The yield of enallenes does not exceed 30% in this instance.

Diethylcalcium[24] and diethylbarium[25] add similarly to the above dienynes. Demetallation of the adducts formed gives conjugated enallenes in 25–30% yield. On the other hand, the use of organolithium reagents in the reaction with dienynes (the method of Petrov and Kormer[15-19]) makes it possible to obtain conjugated enallenes in 70–80% yield.

However, there are certain limitations imposed by the very nature of the method, which makes it possible to synthesise only disubstituted enallenic hydrocarbons in which the number of carbon atoms in the chain is not less than eight‡.

(b) The Interaction of Organolithium Compounds with Tertiary Enynyl Halides and Ethers

On treatment with alkyl-lithium, tertiary ethers and chlorides having the general formula (XXXI) give rise to conjugated enallenic hydrocarbons (XXVIII) together with cumulenes and allenes[19,26]:

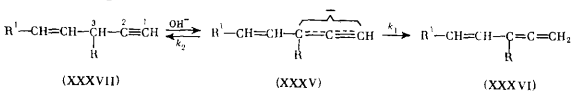


The first stage of the process consists of the 1,4-addition of the alkyl-lithium to the conjugated enyne system of compound (XXXI) with formation of the lithioallene (XXXII). The subsequent reaction of the latter leads to the formation of hydrocarbons (XXXIII) (pathway *a*), (XXVIII) (pathway *b*), or (XXXIV) (pathway *c*). The dependence of the yield of the conjugated enallene (XXVIII) on various factors has been demonstrated in relation to the interaction of the enyne ether (XXXI, X = OCH_3) with organolithium reagents. The most important of these are as follows: solvent polarity, the nature of the alkyl group in the alkyl-lithium, and reaction temperature. It has been shown that a high polarity of the medium leads to the preferential formation of the enallene (XXVIII), because it promotes a greater ease of the dissociation of the C–O bond in the ether. Thus the above ether interacts with n-butyl-lithium in THF at −60°C to form the enallenic hydrocarbon (XXVIII) with a small admixture of the cumulene (XXXIII), while in isopentane the cumulene is the exclusive product. The formation of the cumulene (XXXIII) is fully suppressed on raising the temperature to 0–30°C. In this case the reaction products are the enallene (XXVIII) (in 60% yield) and the hydrocarbon (XXXIV). Higher yields of compound (XXVIII) when the reaction is carried out in ether at −60°C are achieved by using an alkyl-lithium containing secondary or tertiary and not primary alkyl groups.

The influence of the C–O bond strength on the yield of the enallene (XXVIII) in the reactions of tertiary enynyl ethers with alkyl-lithium was discovered on comparing the products of the interaction of n-butyl-lithium with methoxy- and butoxy-derivatives of the hexenyne (XXXI, X = OCH_3 or OC_4H_9). As a result of the greater strength of the C–O bond in the latter ether, the reaction involving the elimination of lithium butoxide in the intramolecular conversion of the adduct (XXXII) predominates over the elimination of butyl alcohol. This is accompanied by the preferential formation of the cumulene (XXXIII). The reaction of the chloride (XXXI, X = Cl) with ethyl-lithium and n-butyl-lithium (in ether, between −30° and −40°C) leads to a mixture of the enallene (XXVIII) in 10–15% yield and the cumulene (XXXIII) in 20–30% yield.

3. THE PROTOTROPIC REARRANGEMENT OF NON-CONJUGATED ENYNE HYDROCARBON (ALK-1-EN-4-YNES)

Bertrand and coworkers developed a preparative method for the synthesis of conjugated enallenic hydrocarbons by the prototropic rearrangement of alk-1-en-4-ynes[12,27,28]. The rearrangement is catalysed by a base, which attacks the active methylene group of the enyne with formation of the ambident carbanion (XXXV). The stabilisation of the latter by the addition of a proton to the $C_{(1)}$ or $C_{(3)}$ atom leads to the enallene (XXXVI) or to the initial enyne (XXXVII) respectively:



(a) R=R¹=H; (b) R=H, R¹=CH_3; (c) R=H, R¹= iso-C_3H_7;
(d) R=CH_3, R¹=H; (e) R=CH_3, R¹=CH_3; (f) R=H, R¹=C_2H_5;
(g) R=n-C_3H_7, R¹ = H.

The proposed mechanism of the rearrangement[28] has been fully confirmed[29-31] in a study of the kinetics and in the determination of the thermodynamic parameters of the process involving enyne hydrocarbons (XXXVII, a–e) substituted in different ways. It has been established that the rate of conversion of the carbanion (XXXV) into the enallene (XXXVI) is many times higher than the rate of its conversion into the initial enyne (XXXVII), i.e. $k_1 \gg k_2$. The application of ultraviolet spectroscopy in combination with gas–liquid chromatography (GLC) made it possible to follow the content in the reaction mixture of both the initial enyne and the enallene formed and to establish that the rate of this reaction may be described by the second-order equation

$$v = k\,[OH^-][\text{alk-1-en-4-yne}].$$

In conformity with the proposed mechanism, the activation energy $E^{\neq}$ and activation enthalpy $\Delta H^{\neq}$ of the isomerisation of the enynes (XXXVIId) and (XXXVIIe), containing the alkyl substituent at the $C_{(3)}$ atom, are much higher than for compound (XXXVII, a–c).

In all the cases investigated the activation entropy $\Delta S^{\neq}$ is negative owing to the restriction in the transition state of free rotation about the $C_{(2)}$–$C_{(3)}$ bond due to the change in the hybridisation of the $C_{(3)}$ atom. The latter promotes a certain degree of separation of the substituents at $C_{(3)}$ owing to the increase of the valence angle resulting in higher values of $\Delta S^{\neq}$ for the isomerisation of the enynes (XXXVIId) and (XXXVIIe) compared with the hydrocarbon unsubstituted at $C_{(3)}$ [$\Delta S^{\neq}$ = −5.1 e.u. for the reaction (XXXVIId) → (XXXVId) and −45.6 e.u. for (XXXVIIa) → (XXXVIa)]. The transition of the $C_{(3)}$ atom from the sp^3

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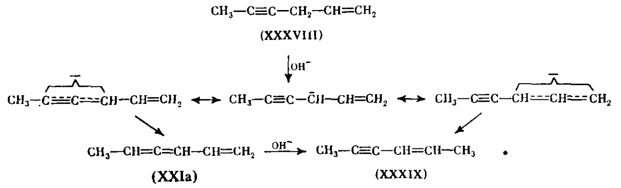
‡ Methyl-lithium does not add to conjugated dienynes[19].

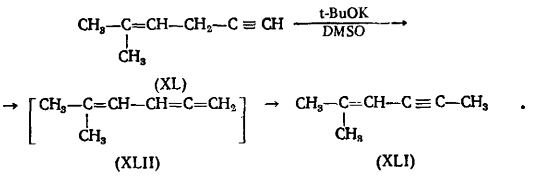
to the sp^2 state on formation of the carbanion (XXXV) greatly reduces the steric interaction of the methyl and ethynyl groups of the *cis*-isomer of the enyne (XXXVIIb), as a result of which the rate of isomerisation of the latter to the enallenic hydrocarbon exceeds by a factor of 3 the rate of isomerisation of the *trans*-isomer ($\Delta S^{\neq}_{cis} > \Delta S^{\neq}_{trans}$).

The intermediate formation of the carbonion (XXXV) explains the stereospecificity of the prototropic rearrangement of alk-1-en-4-ynes in the course of which the configuration of the double bond is maintained. It has been established for a large number of compounds that the above rearrangement takes place smoothly when alk-1-en-4-ynes are refluxed for 3–4 h with a 5% methanolic solution of NaOH, which results in the formation of enallenes with a high degree of purity[27,30].

In contrast to this, the prototropic rearrangement of hex-1-en-4-yne (XXXVIII), carried out under the same conditions, leads to the formation of a mixture of the enallene (XXIa) and the conjugated enyne (XXXIX), the latter being the main reaction product[32]. At 112°C the hydrocarbon (XXXVIII) is converted quantitatively into the enyne (XXXIX). The study of the time course of this process showed that in this case too the reaction takes place with participation of the enallene (XXIa), which isomerises rapidly at the given temperature to the enyne (XXXIX). It has been shown that the enallene is not a necessary precursor of the latter and that direct isomerisation of the initial hexenyne into the enyne (XXXIX) also occurs. Thus the reaction takes place as a parallel-consecutive process in conformity with the mechanism



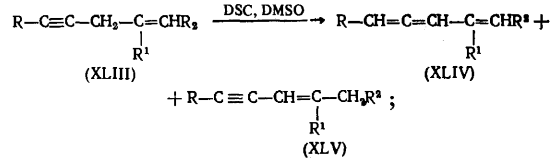
When 2-methylhex-2-en-5-yne (XL) was treated with t-BuOK in dimethyl sulphoxide (DMSO), the conjugated enyne (XLI) was the only product[33]. It has been suggested[33] that the intermediate enallene (XLII) is converted under the experimental conditions into the enyne (XLI) via the classical mechanism of the Favorskii allene–acetylene rearrangement:



$$\underset{(XL)}{CH_3{-}\underset{CH_3}{\underset{|}{C}}{=}CH{-}CH_2{-}C{\equiv}CH} \xrightarrow[DMSO]{t\text{-}BuOK} \underset{(XLII)}{\left[CH_3{-}\underset{CH_3}{\underset{|}{C}}{=}CH{-}CH{=}C{=}CH_2\right]} \rightarrow \underset{(XLI)}{CH_3{-}\underset{CH_3}{\underset{|}{C}}{=}CH{-}C{\equiv}C{-}CH_3}\ .$$

The unstable enallene (XLII) can be obtained[33] by carrying out the reaction under the conditions proposed by Bertrand.

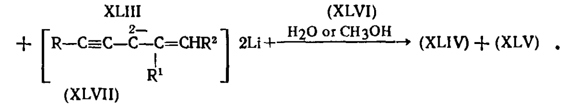
The instantaneous isomerisation of alk-1-en-4-ynes (XLIII) in DMSO, catalysed by the dimethylsulphenyl carbanion (DSC), has been investigated[34] and it has been established that the conjugated enallenes (XLIV) can be obtained only when alk-1-en-4-ynes containing a symmetrically substituted double bond, as in compounds (XLIII, c, d), are used. The conjugated enynes (XLV) are obtained by the isomerisation of the enynes (XLIII, a, b, e, f, g) with a terminal C=C bond under the same conditions, as a result of the subsequent prototropic transformation of the enallenes formed:



$$\underset{(XLIII)}{R{-}C{\equiv}C{-}CH_2{-}\underset{R^1}{\underset{|}{C}}{=}CHR_2} \xrightarrow{DSC,\ DMSO} \underset{(XLIV)}{R{-}CH{=}C{=}CH{-}\underset{R^1}{\underset{|}{C}}{=}CHR^2} + \underset{(XLV)}{R{-}C{\equiv}C{-}CH{=}\underset{R^1}{\underset{|}{C}}{-}CH_2R^2}\ ;$$

(a) $R=C_6H_5$, $R^1=R^2=H$; (b) $R=C_6H_5$, $R^1=CH_3$, $R^2=H$; (c) $R=C_6H_5$, $R^1=H$, $R^2=CH_3$; (d) $R=R^2=C_6H_5$, $R^1=H$; (e) $R=t\text{-}C_4H_9$, $R^1=R^2=H$; (f) $R\text{-}t\text{-}C_4H_9$, $R^1=CH_3$, $R^2=H$; (g) $R=n\text{-}C_6H_{13}$, $R^1=CH_3$, $R^2=H$.

Klein and Brenner described[34–36] the metallation of alk-1-en-4-ynes (XLIII) with butyl-lithium in ether at −90°C, leading to the intermediate formation of the mono- and di-lithio-derivatives (XLVI) and (XLVII). Protonation of the latter leads to a mixture of conjugated enallenes (XLIV), enynes (XLV), and initial compounds[34,35]:



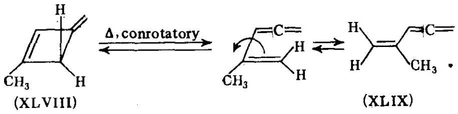
$$\underset{XLIII}{R{-}C{\equiv}C{-}CH_2{-}\underset{R^1}{\underset{|}{C}}{=}CHR^2} \xrightarrow[ether\ \ 90^\circ]{BuLi} \underset{(XLVI)}{\left[R{-}C{\equiv}C{-}\bar{C}H{-}\underset{R^1}{\underset{|}{C}}{=}CHR^2\right]} Li^+ + \underset{(XLVII)}{\left[R{-}C{\equiv}C{-}\overset{2-}{C}{-}\underset{R^1}{\underset{|}{C}}{=}CHR^2\right]} 2Li^+ \xrightarrow{H_2O\ or\ CH_3OH} (XLIV) + (XLV)\ .$$

The composition of the reaction mixture depends on the reaction conditions and also on which lithio-derivative, (XLVI) or (XLVII), is protonated[35].

4. PERICYCLIC REACTIONS

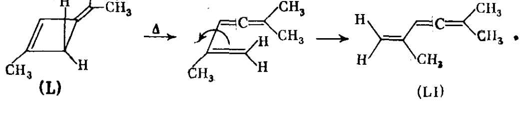
(a) Electrocyclic Transformation of Methylenecyclobutenes

The thermal conversion of methylenecyclobutenes into enallenes is analogous to the electrocyclic conversion of cyclobutenes into butadienes[37]. The opening of the ring of methylenecyclobutenes, which has a 4π-electron system, under thermally controlled conditions is conrotatory[38] and leads to the formation of enallenic hydrocarbons. For example, the pyrolysis (at 350–400°C) of 1-methyl-3-methylenecyclobutene (XLVIII) yielded 2-methylpenta-1,3,4-triene (XLIX):[39]



The process is reversible; the equilibrium reaction mixture contains ~51% of the enallene (XLIX) and ~49% of the methylenecyclobutene (XLVIII). It has been noted that[39] the latter is thermally more stable than alkylcyclobutenes as a result of the stabilising influence of the exocyclic C=C bond.

3-Isopropylidene-1-methylcyclobutene (L) is similarly converted into 2,5-dimethylhexa-1,3,4-triene (LI):[40]

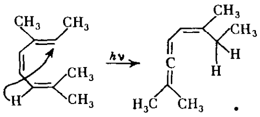


Data indicating the reversibility of this process are lacking; it was carried out by injecting compound (L) into the evaporator of the chromatograph (at 340°C) and trapping the reaction product (yield 45–55%) in a cooled trap.

Since methylenecyclobutenes are not readily available, this method of synthesis of conjugated enallenic hydrocarbons cannot be regarded as preparative.

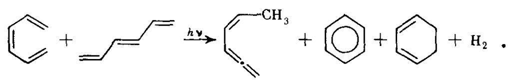
(b) The Sigmatropic Rearrangement of Conjugated Trienes

Conjugated enallenes are formed as a result of the photochemical sigmatropic rearrangement of conjugated trienes. This reaction includes a [1,5]-shift of hydrogen, which is symmetry-allowed as an antarafacial displacement^{41}. According to Crowly's data^{42,43}, the photolysis of allo-ocimene (LII) gives a 37% yield of the unstable enallene (LIII):



(LII) (LIII)

The enallene (IX), cyclohexa-1,3-diene (LV), benzene, and hydrogen have been obtained as the main reaction products by the vapour-phase photolysis of a mixture of the geometrical isomers of hexa-1,3,5-triene (LIV):^{44}



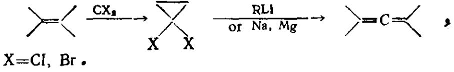
(LIV) (IX) (LV)

Similar products are obtained in the photolysis of cyclohexa-1,3-diene (LV).^{45,46} The enallene (IX) was obtained in this instance as a result of the electrocyclic conversion of the cyclohexadiene (LV) into the conjugated triene (LIV) ^{47} and the [1,5]-sigmatropic rearrangement of the latter.

The isomerisation of conjugated trienes to conjugated enallenes is of considerable interest, since it may be responsible for the biogenic synthesis of natural enallenes^{42}.

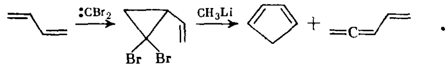
5. DEHALOGENATION OF *GEM*-DIHALOGENOCYCLOPROPANES

The dehalogenation by organolithium reagents$^{48-52}$ or active metals^{53,54} of *gem*-dihalogenocyclopropanes, obtained by the addition of dihalogenocarbenes to olefins, is one of the best methods of synthesising allenes:

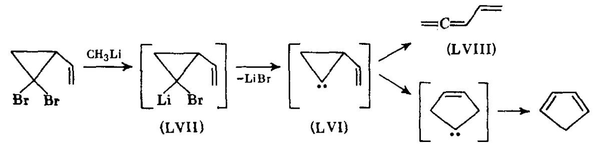


X=Cl, Br.

It might have been expected that conjugated enallenic hydrocarbons can also be synthesised from conjugated dienes by the above procedure. However, Skatteboel showed^{55,56} that, when *gem*-dibromovinylcyclopropanes are treated with methyllithium, cyclopentadienes are formed in 70–90% yield together with only small amounts of enallenic compounds:



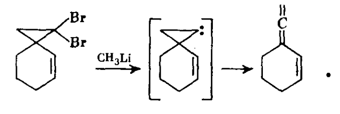
This anomalous course of the reaction can be tentatively^{55} regarded as a result of reactions of cyclopropylidene [the carbene§ (LVI)], generated when lithium bromide is eliminated from the intermediate (LVII). Two products of the above reaction—the enallene (LVIII) and the cyclopentadiene (LIX)—correspond to two different pathways in the transformation of the above carbene. On the one hand, it has been firmly established^{48,51,59} that cyclopropylidene can be converted directly into allene as a result of ring opening. On the other hand, there is a possibility of an intramolecular interaction of the carbene with the double bond, leading to a new carbene (LX). The latter is stabilised by forming the cyclopentadiene (LIX):



(LVII) (LVI) (LX) (LIX)

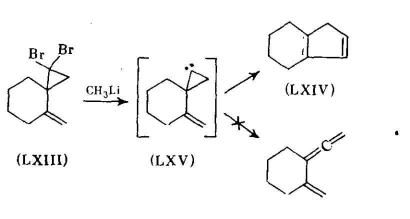
It has been shown^{60} that the preferential formation of an enallene or cyclopentadiene in the above reaction depends on the strain energy in the system formed and the stereochemistry of the intermediate cyclopropylidene. The *s-cis*-conformation of the latter promotes its intramolecular interaction with the double bond and hence the formation of the cyclopentadiene. The *s-trans*-conformation of cyclopropylidene (LVI) favours the direct opening of the three-membered ring with formation of the enallene.

The foregoing findings have been confirmed by the synthesis of the enallene (X), without an admixture of a cyclopentadiene derivative, from the dibromo-compound (LXI), which is an isomer with a rigidly fixed *s-trans*-structure and which gives rise to the intermediate cyclopropylidene (LXII) having the same conformation:



(LXI) (LXII) (X)

It has also been established that the dibromo-compound (LXIII) gives rise exclusively to the cyclopentadiene (LXIV) under the above conditions, which is promoted by the *s-cis*-conformation of the intermediate cyclopropylidene (LXV):



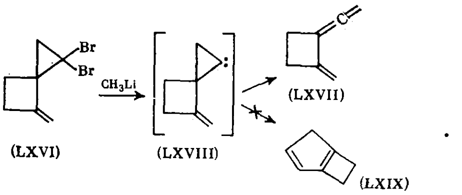
(LXIII) (LXV)

From this point of view, the formation of a mixture of enallenes and cyclopentadienes has been explained logically^{55} by the fact that the initial *gem*-dibromovinylcyclopropanes were mixtures of the *s-cis*- and *s-trans*-conformers.

The adduct of the carbene CBr_2 and 1,2-dimethylenecyclobutane (LXVI) reacts with CH_3Li to form exclusively the enallene (LXVII), despite the fact that this compound

§ It has been suggested^{57,58} that the cyclopropylidene obtained under these conditions is not a free carbene, but forms part of a carbene–lithium halide complex.

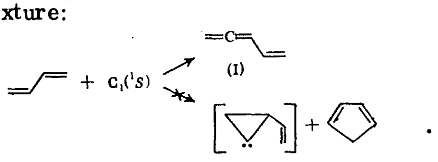
and the cyclopropylidene (LXVIII) are *s-cis*-conformers[60]:



(LXVI) (LXVIII) (LXVII) (LXIX)

The formation of the cyclopentadiene derivative (LXIX) is prevented in this case by the high strain energy of the system.

The data of Skell and Engel[61] are of theoretical interest in connection with the problem of the intermediate formation of cyclopropylidene as the precursor of enallene. It has been established that the reaction of buta-1,3-diene with a carbon atom in the metastable ^1S energy state in a neopentane matrix gives rise to penta-1,2,4-triene (I) only. The cyclopentadiene (LXX) is absent from the reaction mixture:



(I) (LXXV) (LXX)

It follows from calculations[62] by the MINDO/2 method that the activation energy for the opening of the cyclopropylidene (LXXI) ring to give the allene (LXXII) is much higher than the activation energy for the formation of strained systems such as spiropentane (LXXIII) and cyclopropene (LXXIV):


(LXXI)

$=C=$ (LXXII)


(LXXIII)

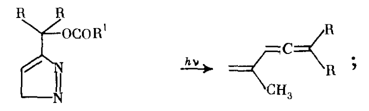

(LXXIV) .

The ring strain energy in cyclopentadiene (LXX) is less than the strain energies in the above system, as a result of which its formation from the postulated intermediate cyclopropylidene (LXXV) apparently requires a smaller activation energy than the formation of enallene (I).

The fact that cyclopentadiene (LXX) is not formed in the reaction under consideration rules out, in our view, the possibility of the formation of enallene (I) from the cyclopropylidene (LXXV)[¶].

6. SPECIFIC METHODS OF SYNTHESIS

Penta-1,2,4-triene is formed on dehydrobromination of 1,4-dibromopent-2-ene[63]. The latter is a readily available product of the bromination of piperylene. The mixture formed on dehydrobromination of the hydrocarbon contains 12.3% of enallene. 2,5-Dimethylhexa-1,3,4-triene has been obtained by a prototropic rearrangement from 2,5-dimethylhexa-2,3,4-triene under the influence of sodium methoxide or hydride[64]. It has been established[65] that the reaction mixture formed on solvolysis of 1-chloromethylene-2,2-dimethylcyclopropane contains 9% of 2-methylpenta-1,3,4-triene. 2,5-Dimethylhexa-1,3,4-triene (LXXVI) and 5-ethyl-2-methylhepta-1,3,4-triene (LXXVII) are obtained in 5% yield on photolysis of the pyrazolenine derivatives (LXXVIII, a, b) and (LXXIX) respectively[66]:

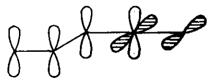


(LXXVIII): (a) $R = R^1 = CH_3$, (b) $R = CH_3, R^1 = C_2H_5$; (LXXIX): $R = C_2H_5$, $R^1 = CH_3$.

(LXXVI): $R = CH_3$; (LXXVII): $R = C_2H_5$

III. PHYSICAL PROPERTIES

The characteristics of the physical properties of the conjugated enallenic hydrocarbons are due to two factors: the cumulation of bonds and conjugation. According to the molecular orbital theory, the planes of two cumulated bonds are mutually perpendicular and the central carbon atom of the allene group, which is in the *sp*-hybridised state, is located on the same straight line with the extreme sp^2-hybridised carbon atoms in this group. Owing to the non-coplanarity of the cumulated bonds, only one of them can be involved in π–π conjugation with the α-ethylenic bond of enallene: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The conjugation[†] of the double bonds in enallenic hydrocarbons is manifested most clearly by the considerable increase of molecular refraction, by the increased magneto-optical molecular rotation, and by the intense absorption in the ultraviolet spectrum, characteristic of conjugated dienes.

1. MOLECULAR REFRACTION

Among all the allenic compounds without an additional double bond in the molecule, only disubstituted allenes with strongly branched groups exhibit a significant exaltation of molecular refraction (ΔMR).[68] It has been suggested[67] that the latter is due to the $\sigma - \pi$ conjugation of the substituents with the coplanar double bond of the allene group and does not exceed unity as a rule. The occurrence of $\pi - \pi$ conjugation in enallene molecules is responsible for the higher values of ΔMR of these compounds, which reach 2.5 in individual instances (Table 5).

2. MAGNETO-OPTICAL MOLECULAR ROTATION

According to Labarre's data[69,70], the experimental magneto-optical molecular rotations (MOMR) of conjugated enallenic compounds greatly exceed the calculated values. Unfortunately penta-1,2,4-triene is the only enallene whose properties have been investigated. Other data quoted in the above reports refer to conjugated enallenic alcohols. However, since the OH group does not influence the magneto-optical properties of these compounds significantly,

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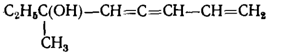
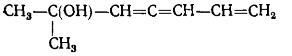
[¶] We have in mind "free" cyclopropylidene generated in the absence of Lewis bases.

[†] The specific influence of the cumulation of bonds on the physical properties of allenes has been described in an extensive review[67].

one may assume that the MOMR exaltation is due to the conjugated enallene group and amounts to ~110 μrad, as can be seen from the data in Table 3.

Table 3. The magneto-optical properties of enallene structures.

Compound	A^*, μrad	B^*, μrad	$E^*=A-B$, μrad
$CH_2=CH-CH=C=CH_2$	664	559	+105
$C_2H_5CH(OH)-CH=C=CH-CH=CH-CH_3$	965	854	+111
 $C_2H_5\underset{\displaystyle CH_3}{\underset{\vert}{C}}(OH)-CH=C=CH-CH=CH_2$	985	882	+103
 $CH_3-\underset{\displaystyle CH_3}{\underset{\vert}{C}}(OH)-CH=C=CH-CH=CH_2$	935	816	+119

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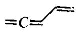
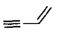
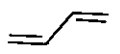
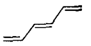
* A is the experimental MOMR, B the calculated MOMR, and E the exaltation of MOMR.

Table 4. The magneto-optical properties of certain conjugated systems.

Conjugated system	E_{av}, μrad	Designation	Conjugated system	E_{av}, μrad	Designation
	+110	E_1		+63	E_3
	+119	E_2		+211	E_4

Labarre[70] also quotes the MOMR exaltations for certain other conjugated systems, which makes it possible to compare them with the values of E found for conjugated enallenes (Table 4). It also follows from the data in Table 4 that E_1 is close to E_2, but differs sharply from E_4. This finding constitutes additional confirmation of the fact that only one C=C bond in the cumulated system of enallene is involved in conjugation. The MOMR exaltation can also serve as a criterion whereby one can distinguish the conjugated enallene system from the conjugated triene and enyne system.

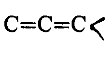
3. ULTRAVIOLET, INFRARED, AND ^{1}H NMR SPECTRA

Ultraviolet Spectra

The ultraviolet absorption spectra are widely used to investigate conjugated enallenic hydrocarbons. As expected, the conjugated enallene group behaves as a chromophore similarly to the conjugated diene system, exhibiting an intense absorption in the range 215–230 nm ($\epsilon \simeq 20\,000$) depending on the nature and number of substituents (Table 5). The absorption is due to a $\pi-\pi^*$ electronic transition.

Infrared Spectra

Because of the presence of characteristic intense absorption bands in the infrared, conjugated enallenic hydrocarbons can be reliably identified or detected in a mixture of unsaturated hydrocarbons by infrared spectroscopy. The infrared spectra of these compounds contain absorption bands characteristic of the allene group[71-73] and a conjugated double bond. The bands associated with the allene group include one in the range 1930–1950 cm^{-1} due to the assymetric stretching vibrations of the –C=C=C– system, a band in the region of 850 cm^{-1} due to the out-of-plane deformation vibrations of the C–H bonds of the terminal



$C=C=C\langle{}^{H}_{H}$

group (overtone at ~1700 cm^{-1}), and absorption at 875 cm^{-1} due to the analogous vibrations of the C–H bonds of the symmetrically disubstituted allene group. The last band is frequently not resolved or appears as a shoulder on the much more intense band close to it and due to the deformation vibrations of the C–H bond of the terminal α-ethylene group. On the other hand, the absorption band at 850 cm^{-1} is of great analytical value and its presence in the spectrum confirms reliably the presence of a terminal allene group in the enallene molecule.

The stretching and deformation vibration frequencies of the α-ethylenic bond in conjugated enallenes are the same as the corresponding vibration frequencies of the conjugated C=C bond in diene hydrocarbons. As an example, one may quote the characteristic positions in the spectrum in the range 1600–1640 cm^{-1} of the band due to the stretching vibrations of the α-ethylenic bond in enallenes[16,19].

Proton Magnetic Resonance Spectra

The ^{1}H NMR spectra of conjugated enallenes are complex and their interpretation is frequently difficult. It has been established[74] that the protons of the allene group located in the positive part of the anisotropy cone are subjected to a positive shielding effect and because of this their signals appear in a stronger field compared with the signals of olefinic protons. Among all the protons of the allene group, the H_A protons, attached to the atoms involved in the double bond of this group, which is non-coplanar with the α-ethylenic bond of the enallene (δ_{H_A} = 4.8 p.p.m.), absorb in the strongest field. The signal in the weakest field (δ_{H_B} = 5.9–6.3 p.p.m.) corresponds to the H_B proton[27]:

.

A characteristic feature of enallenic hydrocarbons and of all allenes is the occurrence of a strong proton–proton interaction via the allene system, which can be accounted for by the interaction of the σ electrons of the C–H bond and the π electrons of the double bond, which are in the same plane[67].

The physical properties of conjugated enallenic hydrocarbons are compiled in Table 5.

Table 5. Conjugated enallenic hydrocarbons.

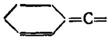
Overall formula	Hydrocarbon*	B.p., °C (pressure, mmHg)	n_D (t, °C)	d_4 (t, °C)	ΔMR_D	Ultraviolet absorption		Method of synthesis**	References
						λ_{max}, nm	ϵ_{max}		
C_5H_6	$CH_2{=}C{=}CH{-}CH{=}CH_2$	48.0—48.5 (760)	1.4685 (25)	0,7133 (25)	1.85	225	13 100	3	27,12,28
	ditto	49	1.4719 (19)	0.7174 (19)	—	—	—	(1*b*)	11
	»	47.5—48.0	1.4750 (18)	—	—	216.5	15 600	1*a*, 5, (6)***	3,6,55, (63)
C_6H_8	$CH_2{=}C{=}CH{-}CH{=}CH{-}CH_3$	80 (760)	1,4790 (25)	0.749 (25)	1.80	228	18 000	3, 1*a*, (4*b*)	27,12,28, 5, (6,44—46)
C_6H_8	$CH_3{-}CH{=}C{=}CH{-}CH{=}CH_2$	84—85 (775)	1.4861 (20)	0,7449 (20)	2.37	214	22 050	3, (1*a,b,c*)	32, (6,14)
C_6H_8	$CH_2{=}C{=}\underset{CH_3}{C}{-}CH{=}CH_2$	71 (760)	1.4780 (20)	0.725 (20)	—	226	11 500	3, 1*a*, (5)	27,5, (6,55)
C_6H_8	$CH_2{=}C{=}CH{-}\underset{CH_3}{C}{=}CH_2$	—	—	—	—	220	17 380	4*a*, (6)	39, (65)
C_7H_{10}	$CH_2{=}C{=}\underset{CH_3}{C}{-}CH{=}CH{-}CH_3$	62 (260)	1,4925 (20)	0.768 (20)	—	228	17 500	3	27
C_7H_{10}	$CH_2{=}C{=}CH{-}CH{=}\underset{CH_3}{C}{-}CH_3$	55 (60)	1.4997 (22)	—	—	230.5	25 700	3	33
C_7H_{10}	$CH_3{-}CH{=}C{=}CH{-}CH{=}CH{-}CH_3$	—	1.4922 (25)	—	—	219	25 400	5, (1*b*)	55, (6,7)
C_7H_{10}	$CH_2{=}C{=}CH{-}CH{=}CH{-}C_2H_5$	56.0—57.5 (98)	1 4800 (24)	0.764 (24)	1.85	227	20 000	3	27,12,28
C_8H_{10}	 $=C{=}CH_2$	—	—	—	—	227	7 350	5, (1*a*)	60, (5,6)
C_8H_{12}	$CH_2{=}C{=}CH{-}CH{=}CH{-}$ iso-C_3H_7	—	1.4786 (20)	0.767 (20)	—	—	—	3	27
C_8H_{12}	$CH_2{=}C{=}C{-}CH{=}CH_2$ n-C_3H_7	56 (180)	1.4765 (20)	0.759 (20)	—	230	23 000	3	27
C_8H_{12}	n-$C_3H_7{-}CH{=}C{=}CH{-}CH{=}CH_2$	37—38 (20)	1.4742 (20)	0.7685 (20)	1.83	—	—	2*a*	15,21,24
	ditto	37—38 (20)	1.4773 (20)	0.7688 (20)	—	—	—	2*a*	25
C_8H_{12}	$CH_3{-}\underset{CH_3}{C}{=}C{=}\underset{CH_3}{C}{-}CH{=}CH_2$	—	1.4857 (20)	0.773 (20)	2.22	—	—	1*b*	10
C_8H_{12}	$CH_3{-}\underset{CH_3}{C}{=}C{=}CH{-}\underset{CH_3}{C}{=}CH_2$	46 (45)	1.4808 (18)	—	—	219	11 700	6	66
	ditto	—	1.4617 (25)	—	—	218	22 000	4*a*	40
	»	—	1.4765 (24)	—	—	220	24 000	5, (6)	55, (64)
C_9H_{14}	n-$C_3H_7{-}CH{=}C{=}CH{-}\underset{CH_3}{C}{=}CH_2$	54—55 (20)	1.4790 (20)	0,7775 (20)	2.21	—	—	2*a*, (2*b*)	16,22,24, 25, (26)
C_9H_{14}	n-$C_3H_7{-}CH{=}C{=}CH{-}CH{=}CH{-}CH_3$	62 (20)	1,4856 (20)	0.7826 (20)	2.44	—	—	2*a*	17,23—25
C_9H_{14}	n-$C_4H_9{-}CH{=}C{=}CH{-}CH{=}CH_2$	56 (20)	1.4742 (20)	0.7755 (20)	—	—	—	2*a*, (1*c*)	21, (14)
C_9H_{14}	$CH_3{-}\underset{CH_3}{C}{=}C{=}\underset{C_2H_5}{C}{-}CH{=}CH_2$	42—44 (20)	1.4825 (20)	0.8021 (20)	—	—	—	1b	9,8
$C_{10}H_{16}$	n-$C_5H_{11}{-}CH{=}C{=}CH{-}CH{=}CH_2$	75—76 (20)	1.4742 (20)	0.7815 (20)	2.03	—	—	2*a*	15,21
$C_{10}H_{16}$	n-$C_4H_9{-}CH{=}C{=}CH{-}CH{=}CH{-}CH_3$	79—80 (20)	1.4837 (20)	0.7869 (20)	—	—	—	2*a*	23
$C_{10}H_{16}$	iso-$C_4H_9{-}CH_2{-}CH{=}C{=}CH{-}CH{=}CH_2$	70.0—70.5 (20)	1,4690 (20)	0.7787 (20)	1.74	—	—	2*a*	15,21
$C_{10}H_{16}$	n-$C_4H_9{-}CH{=}C{=}CH{-}\underset{CH_3}{C}{=}CH_2$	71—72 (20)	1.4790 (20)	0.7834 (20)	2.33	—	—	2*a*	16,22
$C_{10}H_{16}$	$C_2H_5{-}\underset{CH_3}{C}{=}CH{-}CH{=}C{=}\underset{CH_3}{C}{-}CH_3$	23.8—24.1 (0.45)	1.4989 (25)	—	—	225	24 600	4*b*	42,43
$C_{10}H_{16}$	$C_2H_5{-}\underset{C_2H_5}{C}{=}C{=}CH{-}\underset{CH_3}{C}{=}CH_2$	50—52 (11)	1.4819 (18)	—	—	220	15 900	6	66
$C_{10}H_{16}$	iso-$C_3H_7{-}CH_2{-}CH{=}C{=}CH{-}\underset{CH_3}{C}{=}CH_2$	67.5—68.5 (20)	1.4750 (20)	0.7793 (20)	2.24	—	—	2*a*	16
$C_{10}H_{16}$	$CH_3{-}\underset{CH_3}{C}{=}C{=}\underset{n\text{-}C_3H_7}{C}{-}CH{=}CH_2$	56—58 (20)	1.4790 (20)	0.7794 (20)	—	—	—	1*b*	9
$C_{10}H_{16}$	$CH_3{-}\underset{CH_3}{C}{=}C{=}\underset{iso\text{-}C_3H_7}{C}{-}CH{=}CH_2$	42—43 (10)	1.4830 (20)	0.7633 (20)	—	—	—	1*b*	9
$C_{11}H_{18}$	n-$C_6H_{13}{-}CH{=}C{=}CH{-}CH{=}CH_2$	91—92 (20)	1.4738 (20)	0.7841 (20)	2.23	—	—	2*a*	15,21
$C_{11}H_{18}$	n-$C_5H_{11}{-}CH{=}C{=}CH{-}CH{=}CH{-}CH_3$	95—96 (20)	1,4818 (20)	0.7912 (20)	2.52	—	—	2*a*	17,23
$C_{11}H_{18}$	n-$C_5H_{11}{-}CH{=}C{=}CH{-}\underset{CH_3}{C}{=}CH_2$	89.5—90,5 (20)	1.4795 (20)	0.7898 (20)	2.40	—	—	2*a*, (2*b*)	16,22, (26)
$C_{11}H_{18}$	t-$C_4H_9{-}CH_2{-}CH{=}C{=}CH{-}\underset{CH_3}{C}{=}CH_2$	76,5—77,5 (20)	1.4719 (20)	0.7852 (20)	2.52	—	—	2*a*	16
$C_{11}H_{18}$	iso-$C_4H_9{-}CH_2{-}CH{=}C{=}CH{-}\underset{CH_3}{C}{=}CH_2$	83,0—83.5 (20)	1,4762 (20)	0.7853 (20)	2.39	—	—	2*a*	16,22
$C_{11}H_{18}$	$CH_3{-}\underset{CH_3}{C}{=}C{=}\underset{n\text{-}C_4H_9}{C}{-}CH{=}CH_2$	66—68 (12)	1.4770 (20)	0.8181 (20)	—	—	—	1*b*	9
$C_{11}H_{18}$	$CH_3{-}\underset{CH_3}{C}{=}C{=}\underset{C_4H_9\text{-}iso}{C}{-}CH{=}CH_2$	57—58 (10)	1.4870 (20)	0.7950 (20)	—	—	—	1*b*	9
$C_{12}H_{20}$	n-$C_3H_7{-}CH{=}C{=}CH{-}\underset{t\text{-}C_4H_9}{C}{=}CH_2$	77—78 (10)	1,4690 (20)	0.7950 (20)	0.82	—	—	2*a*	18
$C_{12}H_{20}$	n-$C_6H_{13}{-}CH{=}C{=}CH{-}\underset{CH_3}{C}{=}CH_2$	78 (5)	1.4798 (20)	0.7960 (20)	—	—	—	2*a*	22

Table 5 (contd.)

Overall formula	Hydrocarbon*	B.p., °C (pressure, mmHg)	n_D (t, °C)	d_4 (t, °C)	ΔMR_D	Ultraviolet absorption		Method of synthesis**	References
						λ_{max}, nm	ϵ_{max}		
$C_{13}H_{14}$	$C_6H_5{-}CH_2{-}CH{=}C{=}CH{-}\underset{CH_3}{\underset{\vert}{C}}{=}CH_2$	50—51 (0.05)	1.5615 (20)	0.9401 (20)	1.47	—	—	2*a*	20,22
$C_{14}H_{16}$	$m\text{-}CH_3{-}C_6H_4{-}CH_2{-}CH{=}C{=}CH{-}\underset{CH_3}{\underset{\vert}{C}}{=}CH_2$	64—65 (0.06)	1.5530 (20)	0.9796 (20)	—	—	—	2*a*	20,22
$C_{14}H_{16}$	$o\text{-}CH_3{-}C_6H_4{-}CH_2{-}CH{=}C{=}CH{-}\underset{CH_3}{\underset{\vert}{C}}{=}CH_2$	63—64 (0,06)	1.5575 (20)	0.9894 (20)	—	—	—	2*a*	20
$C_{14}H_{24}$	$n\text{-}C_5H_{11}{-}CH{=}C{=}CH{-}\underset{t\text{-}C_4H_9}{\underset{\vert}{C}}{=}CH_2$	104.5—106.0 (10)	1.4690 (20)	0.8032 (20)	1.12	—	—	2*a*	18
$C_{17}H_{16}$	$\alpha\text{-naphthyl}{-}CH_2{-}CH{=}C{=}CH{-}\underset{CH_3}{\underset{\vert}{C}}{=}CH_2$	123—124	1.6150	1.0060	—	—	—	2*a*	20

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*The following enallenes have been characterised solely by spectroscopic methods: 1-methylene-2-vinylidenecyclobutane[60]; 3,4-dimethylpenta-1,2,4-triene[5,6,55]; 3-methylhexa-1,3,4-triene[6,7]; 5-methylhexa-1,3,4-triene[6]; 2,3-dimethylhexa-1,3,4-triene[6,7]; 6,6-dimethylhepta-1,3,4-triene[34]; 4,5-dimethylhepta-2,3,5-triene[6,7]; 2,6,6-trimethylhepta-1,3,4-triene[34]; 1-phenylpenta-1,2,4-triene[34]; 1-ethylidene-2-propenylidenecyclohexane[6,7]; 2-cyclohexenylpenta-2,3-diene[6,7]; 4-methyl-1-phenylpenta-1,2,4-triene[34]; 1-phenylhexa-1,2,4-triene[34]; 3-ethyl-5-methylnona-1,3,4-triene[8]; 5-methyl-3-phenylhexa-1,3,4-triene[8]; trideca-1,3,4-triene[14]; 3,5-diethylnona-1,3,4-triene[8]; 1,5-diphenylpenta-1,2,4-triene[34].

**The designations of the methods of synthesis correspond to those in Section II.

***The references to studies (and to the methods of synthesis employed in them) in which the physical constants of the given enallene are not quoted are enclosed in brackets.

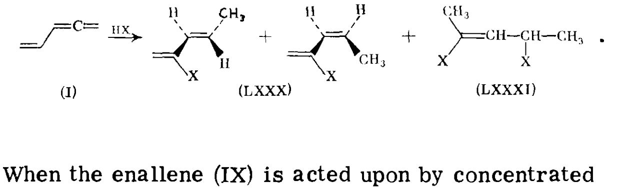
IV. CHEMICAL PROPERTIES

1. ELECTROPHILIC ADDITION

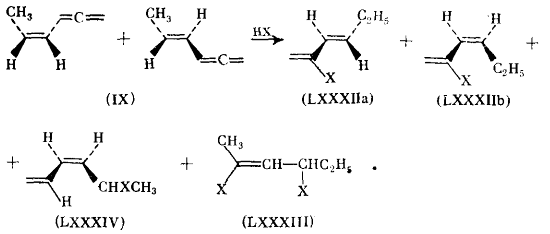
(a) The Addition of Hydrogen Halides[30,75]

When enallene (I) was treated with concentrated HCl, a 3 : 2 mixture of a monoadduct and a diadduct was obtained in 60% yield. The monoadduct is a mixture of the *cis*- and *trans*-isomers of 2-chloropenta-1,3-diene (LXXX, X = Cl) with a threefold excess of the latter isomer. Both geometrical isomers have been isolated by preparative GLC and characterised by infrared, ultraviolet, and ^1H NMR spectroscopy. The diadduct (LXXXI, X = Cl) has been identified as 2,4-dichloropent-2-ene.

The result of the addition of HBr to this enallene is quite analogous as regards the nature of the products and their proportions in the reaction mixture:

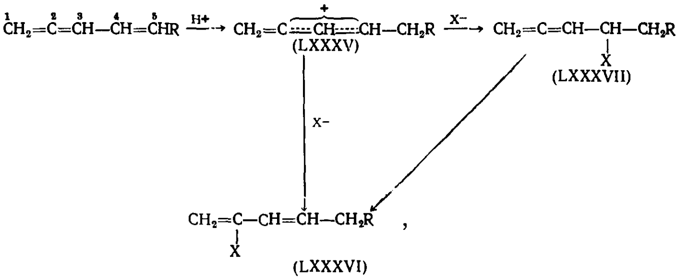


When the enallene (IX) is acted upon by concentrated HCl, a mixture of a monoadduct and a diadduct is again formed. The former, which makes up 65% of the product, is the virtually pure *trans*-isomer of 2-chlorohexa-1,3-diene (LXXXII, a; X = Cl). The *cis*-isomer of this compound has not been isolated, because of its low content in the reaction mixture. The diadduct has the structure of 2,4-dichlorohex-2-ene (LXXXIII, X = Cl):



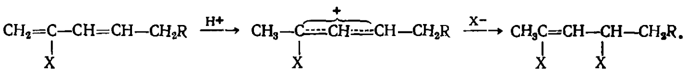
A more complex mixture of adducts was obtained (in 50% yield) when the enallene (IX) was acted upon by hydrobromic acid. According to GLC data, the mixture consists of five monobromides and two dibromides. Three monobromides were isolated by preparative GLC and one of the dibromides was isolated by fractional distillation; 70% of the mixture of monobromides consists of *trans*- and *cis*-2-bromohexa-1,3-dienes in the proportions (LXXXIIa) : (LXXXIIb) = 17 : 3; here X = Br. The third monobromide, which is 5-bromohexa-1,3-diene (LXXXIV, X = Br), was isolated in only a small amount. The structure of 2,4-dibromohex-2-ene (LXXXIII, X = Br) was assigned to the diadduct.

Thus hydrogen halides add to the enallenes (I) and (XIX) in the 1,4-positions in the conjugated ethylene–allene system, and there is also secondary 1,4-addition with formation of diadducts. The reaction mechanism[30,75] consists in the protonation of the $C_{(5)}$ atom of the enallene with formation of the carbonium ion (LXXXV). The latter is attacked by the reagent in the 2- or 4-position, which leads to the halogeno-derivatives (LXXXVI) and (LXXXVII) respectively:



where R = H or CH_3 and X = Cl or Br.

The halogenoallene (LXXXVII) was not detected in the reaction mixture probably owing to the rapid anionotropic rearrangement to the thermodynamically more stable halide (LXXXVI).[75] When a second HX molecule is added, the attack by the proton is directed by the halogen:

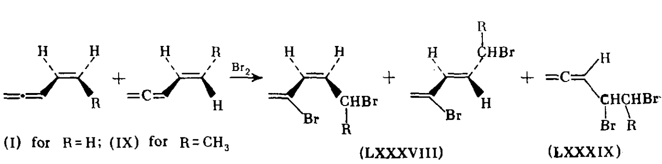


$$CH_2{=}\underset{X}{C}{-}CH{=}CH{-}CH_2R \xrightarrow{H^+} CH_3{-}\overset{+}{\underset{X}{C}}{\cdots}CH{\cdots}CH{-}CH_2R \xrightarrow{X^-} CH_3\underset{X}{C}{=}CH{-}\underset{X}{CH}{-}CH_2R.$$

The interaction of 3-methylpenta-1,2,4-triene and 3-methylhexa-1,2,4-triene with hydrogen halides has also been investigated[30]. However, owing to the rapid polymerisation of these hydrocarbons and the halogeno-derivatives formed, the nature of the processes occurring has not been established.

(b) The Addition of Bromine[30]

The study of the interaction of bromine with conjugated enallenic hydrocarbons is complicated by the difficulty of separating the products. Thus, when penta-1,2,4-triene (I) was brominated, a mixture of three dibromo-derivatives, which could not be separated by distillation, was obtained in 40% yield. According to spectroscopic data, it contained the *cis*- and *trans*-isomers of 1,4-dibromopenta-2,4-diene (LXXXVIII, R = H) and 1,2-dibromopenta-3,4-diene (LXXXIX, R = H):

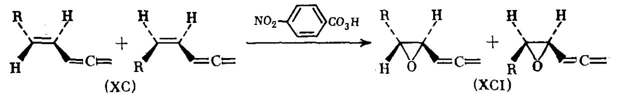


(I) for R=H; (IX) for R=CH_3 (LXXXVIII) (LXXXIX)

The bromination of hexa-1,2,4-triene (IX) also led to a mixture of two dibromo-derivatives (in 30% yield), which could not be separated by distillation. In conformity with spectroscopic data, the structures of the *cis*- and *trans*-isomers of 2,5-dibromohexa-1,3-diene (LXXXVIII, R = CH_3) was attributed to them, the latter being the main product; the 1,2-adduct is not formed in this case.

(c) Epoxidation By Peracids

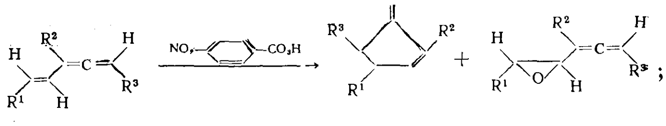
This reaction of conjugated enallenic hydrocarbons was investigated for the first time in relation to the epoxidation of the enallene (XC) by *p*-nitroperbenzoic acid[76]. In all cases the only reaction products are the epoxy-derivatives of α-allenes (XCI), which were not described previously:



(XC) (XCI)

R = H, CH_3, C_2H_5, or n-C_3H_7 .

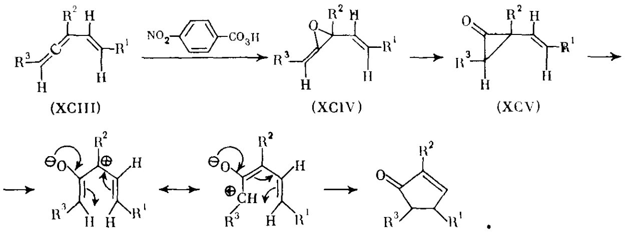
Their geometrical isomers were separated by preparative GLC. It was shown that the ratio of these isomers is determined solely by the ratio of the *cis*- and *trans*-isomers of the initial enallenes, which confirms the stereospecificity of this reaction. It was subsequently established[30,77,78] that the alkylation of the allene group alters the course of the reaction and leads to the formation of the conjugated cyclopentenone (XCII) as the sole or main product:



(XCIII) (XCII) (XCVII)

R^2 or R^3=Alk .

This reaction pathway was explained by the authors as the results of a series of consecutive processes: (1) the epoxidation of the alkylated and therefore fairly nucleophilic allene group of the enallene (XCIII) with formation of the epoxide (XCIV); (2) the tautomeric transformation of the epoxide (XCIV) into the cyclopropanone (XCV); (3) the electrocyclic transformation of the latter into the 1,3-dipole (XCVI) and the subsequent intramolecular 1,3-dipole cycloaddition leading to the formation of the conjugated cyclopentenone (XCII):



(XCIII) (XCIV) (XCV)

(XCVI) (XCII)

Table 6 presents the results of the study of the above reaction.

Table 6. The epoxidation of the conjugated enallenes (XCIII) by *p*-nitroperbenzoic acid[30].

Enallene (XCIII)	Content in reaction mixture, %		Overall yield of (XCII) + (XCVIII), %
	(XCVII)	(XCII)	
(a) $R^1{=}R^3{=}H$, $R^2{=}CH_3$	0	100	60
(b) $R^1{=}R^3{=}H$, R^2 = n-C_3H_7	0	100	60
(c) $R^1{=}R^2{=}CH_3$, R^3 = H(*trans*)	35	65	60
(d) $R^1{=}R^2{=}H$, R^3 = n-C_3H_7	5	95	55

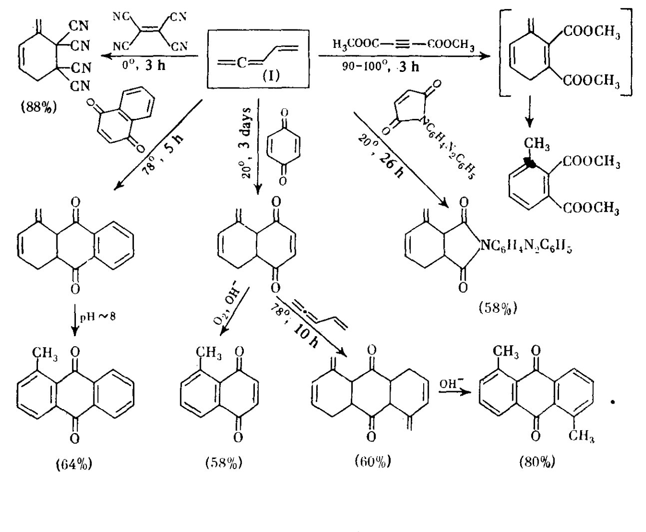
It is noteworthy that, when both the allene group and the α-ethylenic bond are alkylated in the enallene, they are both acted upon, in competition, by the electrophile, which leads to the formation of a mixture of the cyclopentenone (XCII) and the allene epoxide (XCVII). The epoxidation reaction of the enallene (XCIIIc) may serve as an example. It has been shown[30,79] that allene epoxides are valuable starting materials for the synthesis of many hitherto unknown or difficult to obtain compounds such as α- and β-allenic alcohols, vicinal allenic diols, enynyl alcohols, etc. Furthermore, the epoxidation of enallenes by peracids can serve as a method of synthesis of compounds with the hydrindan structure.

2. PERICYCLIC REACTIONS

(a) Thermal Cycloaddition

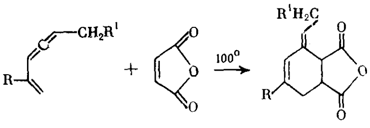
Conjugated enallenes are formally capable of participating in thermal cycloaddition reactions of two types: $[_\pi 2 + {}_\pi 2]$ and $[_\pi 4 + {}_\pi 2]$. A characteristic feature of compounds with a cumulated system of double bonds is known to be the first of the above transformations, which results in the formation of cyclobutane derivatives[80], while dienes with a conjugated system of bonds are involved preferentially in the $[_\pi 4 + {}_\pi 2]$ cycloaddition reaction, which leads to the formation of cyclohexene derivatives. The simultaneous presence in the molecule of the conjugated enallene of cumulated and conjugated diene systems constitutes an interesting problem as regards their competition in the cycloaddition reaction.

The possibility of the involvement of conjugated enallenes in the Diels–Alder reaction, which is a type of $[_\pi 2 + {}_\pi 2]$ cycloaddition, was demonstrated for the first time[3] in relation to the reaction of penta-1,2,4-triene (I) with different dienophiles. This hydrocarbon reacts under mild conditions with tetracyanoethylene and derivatives of maleic and acetylenedicarboxylic acids and quinone. The reactions which have been carried out and the products obtained are indicated schematically below:



Many of the adducts indicated in the above scheme are methylenecyclohexene derivatives, which are difficult to obtain in other ways. The ready aromatisation of certain compounds makes enallene (I) a valuable starting material for the synthesis of aromatic compounds which are difficult to obtain.

Fedorova and Petrov[18] investigated the reactions of the enallenes (XCVIII) and maleic anhydride at 100°C. Homologues of the anhydride of 3-alkylidene-4-cyclohexene-1,2-dicarboxylic acid (XCIX) were obtained in all cases:



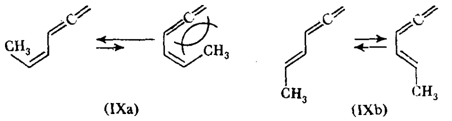
(XCVIII) (XCIX)

(a) $R = CH_3$, $R^1 = C_2H_5$; (b) $R = CH_3$, $R^1 =$ n-C_4H_9;
(c) $R =$ t-C_4H_9, $R^1 = C_2H_5$;
(d) $R =$ t-C_4H_9, $R^1 =$ n-C_4H_9 .

Further condensation does not take place despite the presence in the adduct (XCIX) of a conjugated diene group, which is believed[18] to be due to steric factors.

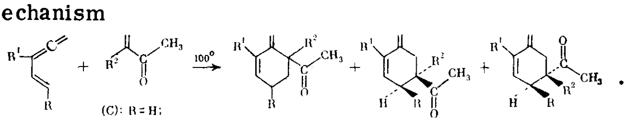
The mechanism of the thermal $[_\pi 4 + {}_\pi 2]$ cycloaddition of conjugated enallenes has been determined in a study of their reactions with but-1-en-3-one (C) and 2-methylbut-1-en-3-one (CI).[30,81,82] It has been shown that the reaction proceeds via a concerted cyclic mechanism, which is symmetry-allowed as a $[_\pi 4_s + {}_\pi 2_s]$ process, in which all the π orbitals are involved suprafacially. A direct consequence of this mechanism is the requirement of a definite, namely cisoid, conformation of the reacting enallene, so that the addition of the dienophile must be preceded by the conversion of the energetically more favourable transoid conformation of the hydrocarbon into the cisoid conformation.

Such transformation of the *cis*-isomer of hexa-1,2,4-triene (IXa) is difficult for steric reasons and it does not therefore react with the above ketones. Under these conditions, the *trans*-isomer of the enallene (IXb) actively interacts with the ketones:



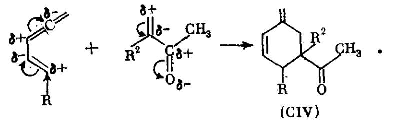
(IXa) (IXb)

The conjugated enallenes (CII) react with $\alpha\beta$-unsaturated ketones as the diene components in accordance with the mechanism



(CII) (C): R = H; (CI): R = CH3 (CIII) (CIV,a) (IVb)

The experimental data obtained are compiled in Table 7. The structures of the products have been reliably demonstrated by spectroscopic methods (infrared, ^{1}H NMR, and ultraviolet), by mass spectrometry, and by their conversion into the corresponding aromatic compounds in order to determine the position of the acetyl group in the adduct which indicates the relative orientations of the dienophile and enallene in the transition state. This orientation is unambiguous and leads to the exclusive formation of the adduct (CIV) subject to the condition that the terminal $C_{(5)}$ atom of the α-ethylenic bond of the enallene (CII) has an alkyl substituent (i.e. $R \neq H$):



(CIV)

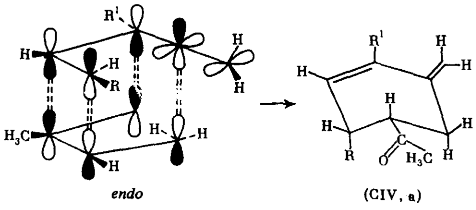
Otherwise a mixture of the adducts (CIII) and (CIV) is formed with the latter greatly predominating. The ratio of the adducts depends little on whether there is an alkyl substituent at the $C_{(3)}$ atom of the hydrocarbon and on whether the C=C bond of the ketone is alkylated, which rules out a zwitter-ionic mechanism of the cycloaddition.

Table 7. The compositions of the reaction mixtures obtained in the interaction of the enallenes (CII) with αβ-unsaturated ketones[82].

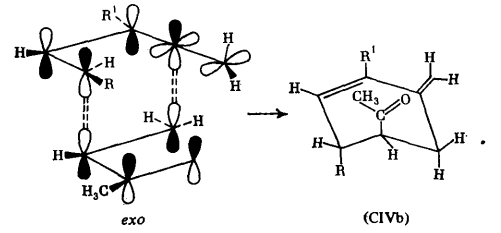
Groups in (CII)-(CIV)			Overall yield of (CIII) + (CIV), %	Fraction of adduct (CIII), %	Fraction of adduct (CIV), %	Fraction of adduct (CIVa) in (CIV), %	Fraction of adduct (CIVb) in (CIV), %
R	R^1	R^2					
H	H	H	60	28	72	—	—
H	CH_3	H	75	20	80	—	—
H	n-C_3H_7	H	70	15	85	—	—
H	H	CH_3	40	21	79	—	—
CH_3	H	H	50	0	100	75	25
iso-C_3H_7	H	H	65	0	100	82	18
CH_3	CH_3	H	75	0	100	80	20
CH_3	H	CH_3	35	0	100	100	0

In the reaction of the enallenes (CII, R ≠ H) with the ketone (C) the adduct (CIV) was obtained as a mixture of the *cis*- and *trans*-isomers, (CIVa), and (CIVb), respectively. It was established that the former is the kinetically controlled product and the latter the thermodynamically controlled product of the reaction. The fact that the kinetically controlled *cis*-adduct greatly predominates (Table 7) supports the concerted mechanism. If a two-stage mechanism operated, the ratio of the geometrical isomers (CIVa) and (CIVb) would have been determined by the thermodynamic equilibrium.

The kinetic control of the ratio of the stereoisomeric adducts in the reaction under consideration can be accounted for on the basis of the Woodward–Hoffmann rules[38], which take into account the interaction between the frontal orbitals of the reacting molecules. The interaction between the lowest unoccupied orbital (LUMO) of the conjugated diene system of the enallene and the highest occupied orbital (HOMO) of the ethylenic system of the αβ-unsaturated ketone in the transition state, with *endo*- and *exo*-dispositions of the reacting molecules, is illustrated schematically below:



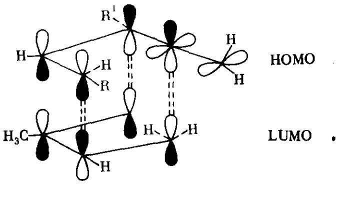
endo (CIV, a)



exo (CIVb)

The more effective overlapping of the π orbitals of the two systems in the case of the *cis*- adduct (*endo*-addition)[‡] leads to a decrease of the activation energy for its formation relative to that for the *trans*-adduct (*exo*-addition). Because of this, the *cis*-adduct (CIVa) is the kinetically controlled main product of the reaction.

An alternative treatment of the interaction of the LUMO of the ethylenic bond of the dienophile and the HOMO of the diene system of the enallene leads to the conclusion that such interaction is energetically less favourable owing to a smaller secondary orbital effect even for the most favourable *endo*-disposition of the reacting molecules:

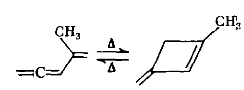


The absence of compounds with the cyclobutane structure among the products shows that, under the experimental conditions, there is no competition between the allene and conjugated groups of the conjugated enallenes, i.e. the reaction proceeds solely via the $[\pi 4_s + \pi 2_s]$ cycloaddition mechanism.

It is noteworthy that this reaction is of great interest for synthesis. The thermal cycloaddition of enallenes to unsaturated ketones can be widely used in the synthesis of monocyclic terpenoids, particularly derivatives of β-phellandrene[30,81]. Furthermore it has been shown[30] that the base-catalysed prototropic rearrangement of certain adducts with structure (CIII) easily leads to cyclic conjugated trienones.

(b) Electrocyclic Reactions

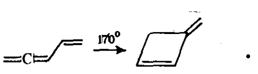
Much interest has been aroused recently by uncatalysed thermal reactions of triene hydrocarbons containing the allene group[84]. The electrocyclic transformation of the latter has become a preparative method for the synthesis of certain exotic cyclic hydrocarbons. However, there are few data concerning the thermal behaviour of conjugated enallenes. It has been established[39] that pyrolysis of 2-methylpenta-1,3,4-triene (XLIX) in pentane at 350–450°C leads to the formation of 1-methyl-3-methylene cyclobutene (XLVIII). With increase of the duration of pyrolysis, the fraction of the hydrocarbon (XLVIII) in the reaction mixture remained constant, which indicated the attainment of equilibrium. The reversibility of the process was also demonstrated by the pyrolysis of methylenecyclobutene (XLVIII) and the discovery that the ratio of the hydrocarbons (XLIX) and (XLVIII) in the reaction mixture remains constant:



(XLIX) (XLVIII)

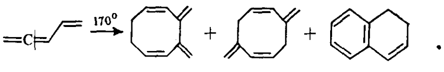
[‡] αβ-Unsaturated dienophiles react with dienes in the cisoid conformation[83].

At 170°C penta-1,2,4-triene undergoes analogous cyclisation to methylenecyclobutene (CV):[85]



(I) (CV)

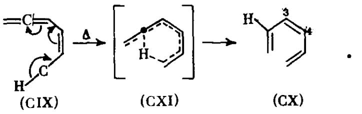
However, the content of the cyclic hydrocarbon (CV) in the reaction mixture does not exceed 10%. The main pathway in the thermal transformation of enallene (I) is its dimerisation, leading to the formation of at least seven hydrocarbons having the composition $C_{10}H_{12}$. Only three have been specified as the most interesting[85]—compounds (CVI), (CVII), and (CVIII):



(I) (CVI) (CVII) (CVIII)

(c) Sigmatropic Rearrangements

Apart from the intramolecular cyclisation discussed above, the thermal transformation of an enallene can involve a sigmatropic rearrangement to a conjugated triene accompanied by a [1,5]-H-shift:

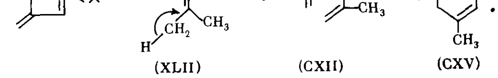


(CIX) (CXI) (CX)

Since this process involves three electron pairs, the synchronous migration of hydrogen takes place suprafacially[86].

The sigmatropic rearrangement of the enallene system (CIX) to the conjugated triene system (CX) is believed to take place[87] as a result of a rearrangement of the orbitals in the six-centre transition state (CXI). The latter is possible only provided that the initial enallene has the *cis*-configuration of the α-ethylenic bond. The experimental observation that the 3,4-bond in the resulting triene (CX) is a *cis*-C=C bond confirms the cyclic process mechanism.

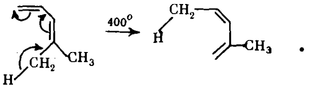
The sigmatropic rearrangement of 5-methylhexa-1,2,4-triene (XLII) takes place similarly[33], the compound being rapidly converted into *cis*-2-methylhexa-1,3,5-triene (CXII) at 135°C:



(XLII) (CXII) (CXV)

A methylenecyclobutene derivative is not formed under these conditions. The above process has an activation energy of 24.6 kcal mole^{-1} and proceeds at an anomalously low temperature.

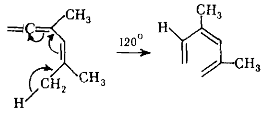
The analogous thermal rearrangement of acyclic conjugated dienes requires much more severe conditions. Thus the sigmatropic rearrangement of 4-methylpenta-1,3-diene (CXIII) to *cis*-2-methylpenta-1,3-diene (CXIV) proceeds at a temperature not less than 400°C (E_a = 32.8 kcal mole^{-1}):[88]



(CXIII) (CXIV)

The thermal transformation of the enallene (XLII) at 330°C leads to the exclusive formation of the cyclohexadiene derivative (CXV), which is a consequence of the intramolecular cyclisation of the hexatriene (CXII), having the *cis*-configuration which favours the electrocyclic process.

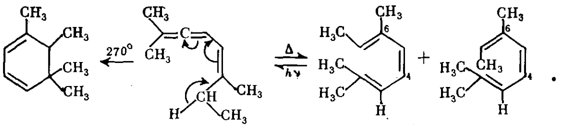
The conjugated enallene (CXVI) rearranges to the conjugated triene (CXVII) at the instant of distillation[33,55]:



(CXVI) (CXVII)

It is of interest to compare the thermally controlled transformation of conjugated enallenes into conjugated trienes with the opposite process which is photochemically controlled. Thus 2,6-dimethylocta-2,3,5-triene (LIII), obtained by the photochemical [1,5]-sigmatropic rearrangement of 2,6-dimethylocta-2,4,6-triene (LII), was reconverted into the initial triene (LIII) after heating for 8 min at 112–114°C as a result of a thermal [1,5]-H-shift (degree of conversion 93%).[42,43] The triene (LII) is formed as a mixture of the 4-*cis*-6-*cis*- and 4-*cis*-6-*trans*-isomers, the latter greatly predominating owing to favourable steric factors. As already mentioned above, the *cis*-configuration of the central double bond of the triene (LII) is a consequence of a cyclic mechanism of the rearrangement.

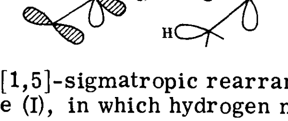
As expected, at a higher temperature (270°C) the enallene (LIII) is converted into the cyclohexadiene (CXVIII):



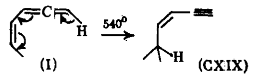
(CXVIII) (LIII) (LII)

It has been established[43] that the 4-*trans*-6-*trans*- and 4-*trans*-6-*cis*-isomers of the hydrocarbon (LII) are formed when the enallene (LIII) is stored for several years at room temperature.

It has been suggested[33] that the unusual ease with which the thermal sigmatropic rearrangement of conjugated enallenes takes place (compared with conjugated dienes) can be accounted for by the specific influence of the allene group. In the case of a [1,5]-H-shift in the enallene the hydrogen atom migrates to the C atom in the *sp* state, which is more electronegative than the C atom in the sp^2 state to which the hydrogen atom migrates in the diene. Furthermore, the sigmatropic rearrangement of the enallene results in the dissociation of the C_{sp^3}–H bond and the formation of a stronger C_{sp^2}–H bond. These effects lead to an appreciable decrease of the process activation energy. The stabilisation of the transition state during the rearrangement of the enallene to a conjugated triene can take place as a result of the partial involvement in the conjugation of the π orbitals of the terminal C=C bond of the allene group:

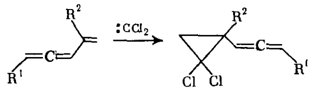


A new type of [1,5]-sigmatropic rearrangement of penta-1,2,4-triene (I), in which hydrogen migrates from the terminal carbon atom of the allene group to the terminal carbon atom of the α-ethylenic bond, was established recently[85]. The rearrangement, occurring at a very high temperature (540°C), results in the formation of pent-2-en-4-yne (CXIX):



(d) Cheletropic Reactions

Conjugated enallenes react with carbenes. This reaction, which belongs to the class of non-linear cheletropic processes[38], has been investigated in relation to the interaction of dichlorocarbene with penta-1,2,4-triene (I)[89] and 2-methylocta-1,3,4-triene (CXX).[90] It was carried out with an equimolar enallene–dichlorocarbene mixture, the dichlorocarbene being generated from t-BuOK and chloroform. It was shown that in both cases the dichlorocarbene attacks the α-ethylenic bonds of enallenes, which shows that it has more pronounced nucleophilic properties than the C=C bonds in the allene group:



(I): $R^1=R^2=H$; (CXXI): $R^1=R^2=H$;
(CXX): $R^1=n\text{-}C_3H_7$, $R^2=CH_3$; (CXXII): $R^1=n\text{-}C_3H_7$, $R^2=CH_3$.

The selective addition of CCl_2 to the α-ethylenic bonds of enallenes (I) and (CXX) resulted in the synthesis of new derivatives of *gem*-dichlorocyclopropane, (CXXI) and (CXXII), containing an allene group conjugated with the cyclopropane ring.

The more marked nucleophilic properties of the α-ethylenic bond of enallene (I), manifested in its reaction with dichlorocarbene, have also been confirmed by the results of the epoxidation of this hydrocarbon with *p*-nitroperbenzoic acid.

3. CATALYTIC HYDROGENATION

Selective stepwise hydrogenation of conjugated enallenes has not been studied. Exhaustive hydrogenation of these compounds proceeds smoothly in the presence of palladium and platinum catalysts, which has been used to demonstrate the structures of many conjugated enallenes[15,17,42,43].

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Practical Applications of Cyclopentadienyl Complexes of Transition Metals

N.S.Kochetkova and Yu.K.Krynkina

The review is devoted to the main practical applications of metallocenes (dicyclopentadienylmetal complexes); the main practical applications of ferrocene and its derivatives are dealt with most widely. The practical utilisation of other cyclopentadienylmetal complexes is only beginning and the number of studies in this field is small. Investigations published in 1977 are considered.
The bibliography includes 162 references.

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I. INTRODUCTION

The practical applications of dicyclopentadienylmetal complexes (metallocenes) have become possible owing to the successful development of synthetic research in this field. Ferrocene, which was discovered little more than 20 years ago, led to the foundation of the chemistry of metallocenes. Despite the fact that the cyclopentadienyl complexes of almost all the metals and many non-metals are known at present, the chemistry of the derivatives of metallocenes has so far been investigated most widely only for ferrocene[1,2]; that of osmocene and ruthenocene began to develop only comparatively recently and this is also true of cobaltocenium, nickelocenium, vanadocenium, etc. salts[2,3]. Derivatives of the dicyclopentadienyl complexes of titanium, zirconium, and to a lesser extent hafnium have been investigated in greater detail[4]. Among monocyclopentadienyl compounds, cyclopentadienylmanganese tricarbonyl (CMT) and cyclopentadienylrhenium tricarbonyl (CRT) have been most thoroughly investigated chemically[4].

The development of synthetic research on mono- and di-cyclopentadienyl derivatives of metals has served as the foundation on which the development of applied research in this field has been based. In the present review, which is devoted to the practical applications of metallocenes, attention is concentrated on the practical utilisation of ferrocene and its derivatives and studies associated with the cyclopentadienyl derivatives of other metals are only touched upon. The review constitutes a continuation of an earlier review[5], which was devoted to the practical applications of ferrocene and its derivatives.

A characteristic feature of the applications of metallocenes, which has become apparent recently, is the possibility of using them in various seemingly opposed fields; for example, ferrocene is used both as an inhibitor of the ageing of polymers and as a catalyst for their self-decomposition; or, for example, partly oxidised ferrocene derivatives are extremely effective semiconductors, while ferrocene serves at the same time as a successful additive in the manufacture of electrical insulators. The conditions used in the employment of metallocenes, their concentration, solvents, conditions of treatment, etc. apparently play a major role; for this reason, the application of such metal complexes requires an extremely careful adherence to the conditions developed for their utilisation. Wide scale studies on the properties of metallocenes involving all chemical and physicochemical methods are necessary; we may note that so far there have been virtually no quantitative investigations.

Studies on the mechanisms of the stabilisation of thermostable polymers under the influence of metal-containing inhibitors are only briefly mentioned in the review.

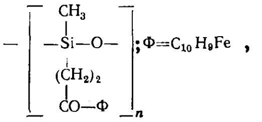
II. THERMO- AND PHOTO-STABILISERS

Effective photostabilisers for polymers, particularly *o*-hydroxybenzoylferrocene (I)[6,7], have been discovered comparatively recently and the possibility of coating spaceships with this compound has been mentioned[8]. The inhibiting effect of the ferrocenyl residue is apparently associated with the ability of compounds of this type to absorb light in both the visible and ultraviolet regions[9]. One cannot rule out the possibility that the effect is also enhanced by the aromatic component of the molecule, since benzoylbenzene derivatives are well known photostabilisers[10]. Other compounds containing the ferrocenyl fragment in the molecule, for example, phenylene substituted in the 4-position, can also serve as thermo- and photostabilisers[11]. Inhibitors of the light-induced ageing of polypropylene have been described[12].

The products of the interaction of diacetylferrocene with formaldehyde, which the authors called "diacetylferrocene-formaldehyde resins", have also been proposed for the modification of textile fibres based on poly(vinyl alcohol), for the improvement of their mechanical properties in spinning, and for the improvement of their resistance to the action of light[13]. The dimethyl ester of ferrocenedicarboxylic acid can likewise serve as a photostabiliser[14]. A decrease in mechanical fatigue strength in the spinning of fibre may be achieved by introducing into acetylcellulose 0.5-1 wt.% of formylferrocene[15], which also imparts resistance to radiation and increases the adhesion of polyamides to rubber[16,17].

Ferrocene has been proposed as a thermostabiliser for polyethylene: tests on shields 2 mm thick (involving heating to 100° C for three days) showed that the tensile strength decreases to 82.2% compared with 69.3% for the control specimen[18]. The addition of small amounts of ferrocene (0.5 wt.%) has a similar effect on ethylene–propene and diene rubbers[19]. A polyethylene film is stabilised in relation to ultraviolet radiation by the addition of 10% of the benzaldehyde–ferrocene copolymer in methylene chloride[20].

Polyferrocenylsiloxanes of the type

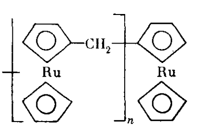


$$-\left[-\overset{\displaystyle CH_3}{\underset{\displaystyle (CH_2)_2-CO-\Phi}{Si}}-O-\right]_n ;\ \Phi = C_{10}H_9Fe\ ,$$

where the side chain contains the same ferrocenyl residue, have been described[5] as absorbers of ultraviolet light and photostabilisers.

Among other ferrocene derivatives proposed as thermostabilisers and antioxidants, *p*-aminoarylferrocenes have been mentioned[21]. Organosilicon derivatives of ferrocene in which the silicon atom is linked directly to the ferrocene ring constitute an interesting group of antioxidant stabilisers for polymers: $C_{10}H_4Fe[Si(CH_3)_3]_2$, $C_{10}H_8Fe[Si.(CH_3)_2OC_2H_5]_2$, $C_{10}H_8Fe[Si(CH_3)_2.OC_8H_{17}]_2$, $C_{10}H_8Fe[Si.(CH_3)_2OC_6H_5]_2$, and $C_{10}H_8Fe[Si(CH_3)_2N(C_2H_5)_2]_2$. In this series the most effective compounds are the diethylaminosilyl derivatives[22], which can be used as antioxidants for heat exchangers in refrigerators[23].

Polymers based on ruthenocene



proved to be resistant to heat and radiation[24]. They have been proposed as special protective coatings.

Two general ways of inhibiting polymer decomposition processes were examined in a recently published review[25]: (1) inhibition of chain processes by introducing into the system substances causing chain termination; (2) the removal from the system of chemical agents (present in the polymer composition or formed as a result of ageing), weak bonds, etc. It is shown in the same review that the deactivation of active centres under the influence of metal-containing inhibitors takes place as a non-chain inhibition process. The $M-C_5H_5$ bond dissociation energy probably constitutes a measure of the thermal stability of the compounds. Thermal decomposition can result in the formation of either pure finely dispersed metals or readily oxidisable products, which are involved in the chain termination reactions in the course of thermochemical degradation.

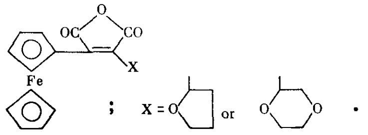
III. DYES AND PHOTOGRAPHIC MATERIALS

Few data on ferrocene dyes have appeared in the literature of recent years: this can be explained primarily by their low stability to light; early studies in this field have already been discussed[5].

Data have been published recently concerning the possibility of using organometallic compounds in photographic and particularly electrophotographic processes. Thus light-sensitive compositions containing organoelemental compounds, particularly cyclopentadienylmetal complexes, have been proposed[26]. An electrophotographic material is obtained by pouring compositions containing photoconductors, polyhalogeno-substituted compounds (for the formation of free radicals under the influence of light), the base form of the dye (for the formation of a sensitising dye under the influence of free radicals) and organoelemental additives onto conducting polyvinyl supports. After preliminary activation of these compositions by light or after pouring the same compositions onto polyvinyl supports and subsequent irradiation of the entire conducting polyvinyl layer with light, a positive image is formed. The material is then charged by a corona discharge source, irradiated with light from a tungsten lamp, and developed using a positive liquid developer, which yields the positive image. Tetraethyl-lead is used as an organometallic additive; cyclopentadienylmetal complexes have been mentioned as possible additives.

Photographic materials based on vinylferrocene, organic halides, and aromatic amines or their derivatives have been recently proposed[27] as photographic materials. A negative image has been obtained on paper following the illumination with light from a mercury lamp of a light-sensitive composition consisting of the styrene–vinylferrocene copolymer, tribromomethane, *p*-nitrophenyl sulphone, and diphenylamine.

Compounds containing the products of the condensation of maleic anhydride with tetrahydrofuran (THF), or 1,4-dioxan have been proposed as antidetonating agents and as inks soluble in organic solvents[28]:



IV. ADDITIVES TO FUELS AND OILS

Derivatives of ferrocene and cyclopentadienylmanganese tricarbonyl serve as regulators of various oxidation processes occurring in the fuel. They can be used as antismoke and anticoking agents, antidetonating agents, and regulators of the rate of combustion, can promote more complete oxidation of the fuel and decrease the amount of harmful exhaust gases resulting from combustion, and can even inhibit combustion processes, imparting fire resistance to the relevant substances. In view of the urgency of all the problems enumerated, the large scale manufacture of fuels of various types, and the importance of the problem of the protection of the environment, the possibility of using metallocenes in this field is of considerable practical interest.

1. Antismoke Additives

Ferrocene, diethylferrocene, tris(acetylacetonato)iron[29], CMT, and polymers based on vinyl-CMT and methyl-CMT have been proposed as antismoke additives to motor fuel[30].

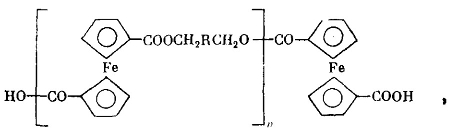
The successful use of organometallic antismoke additives is possible only in those cases where small amounts of the additive to the fuel (0.05–0.1 wt.%) can ensure a very effective increase of the degree of combustion of the fuel and a decrease of the amount of smoke. An increase in the amount of the antismoke additive can lead to other undesirable phenomena–the formation of a deposit on the working components of the engine, etc.

2. Antidetonating Agents

CMT† and ferrocene derivatives are effective antidetonating agents. However, fairly extensive deposit formation accompanying the use of ferrocene derivatives has so far precluded the practical employment of these compounds. Tests on the antidetonating properties of compounds of this class have shown[31,32] that ferrocenylmethyltrimethylammonium iodide, diferrocenylpropenone, and ferrocenylfluorophenylpropenone are most effective. Compounds containing a halogen and nitrogen form the smallest amount of deposit but it was not discovered whether nitrogen oxides are formed in the exhaust gases.

3. Regulators of the Rate of Combustion

Among new studies in this field, mention should be made of polymeric ferrocene-containing substances, for example, the products of the polycondensation of the heteroannular ferrocenedicarboxylic acid and diglycols (IX)[33,34], i.e.



(I)

the copolymers of isopropylferrocene or 1-divinylferrocene with butadiene, isoprene, and chloroprene[35], and the copolymers of butylferrocene with formaldehyde[36] and of vinylferrocene with butadiene[37] or chloroprene[38,39].

An involatile combustion catalyst, obtained by condensing t-butylferrocene with methylal[40] and added to a carboxylate butyl-rubber, the vulcanising agent, ammonium perchlorate, and dioctyl adipate, ensures an increase of the rate of combustion by a factor of 2–2.5.

Intensive research on the elimination of exhaust gases from air is proceeding in various countries. Thus it has been suggested that ferrocene be used as an additive to fuel (0.05 wt.%), which promotes the further combustion of CO to CO_2.[41] Compositions which yield less harmful substances on combustion have been obtained from poly(vinyl chloride), an aliphatic plasticiser, and $CaCO_3$ with small amounts of added ferrocene as well as lead stearate and sulphate.

4. Oxidation Inhibitors

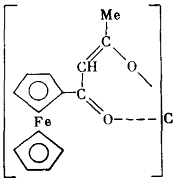
Ferrocene derivatives can serve not only as catalysts but also as inhibitors of oxidation. Thus fire-resistant compositions in which ferrocene and its derivatives are combined with halogen-containing polymeric materials have been proposed in a number of studies[42-44]. For example, fire-resistant shields (2 mm thick) are made from a composition containing polychlorovinyl-bis-(2-ethylhexyl) phthalate, lead sulphate and stearate, ferrocene, and $MgCO_3$. Such shields are also made from ferrocene-containing copolymers with anisyl aldehyde and *pp'*-benzoquinone dioxime combined with butyl-rubber and zinc oxide. Similar fire-resistant compositions, based on polyethylene with added ferrocene, have been proposed[42]. It may be that, oxidation inhibitors are formed from ferrocene and its derivatives on heat treatment in the presence of the components of the given fire-resistant compositions.

5. Accelerators of the Decomposition of Polymers

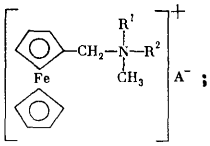
The problem of the contamination of the environment by waste products from the synthesis of polymers, which are difficult to decompose, is now becoming increasingly acute. Ferrocene and its derivatives proved not only to inhibit the ageing of polymers but also to catalyse their decomposition[44].

6. Antistatic Additives to Fuel

The transport of fuel over long distances and its storage for a fairly long time constitute an urgent problem. The necessity to find antistatic additives to fuel arises in this connection. Among ferrocene and CMT derivatives, salt-like compounds containing a chromium atom in addition to iron or manganese atoms have been proposed[45,46]:



It has recently been suggested[47] that alkylammonium salts of the dialkylaminomethylferrocene type be used as antistatic additives[47]:

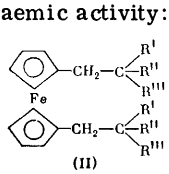


; $R^1 = C_nH_{2n+1}$ ($n = 1-5$), CH_2CH_2OH; $R^2 = C_nH_{2n+1}$ ($n = 1-18$); $A = Cl, Br, I, NO_3, SO_4, MeSO_4$, or ClO_4 .

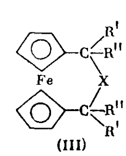
V. MEDICINAL SUBSTANCES

Ferrocene compounds proved to be effective agents in the fight against diseases caused by iron deficiency in the organism, i.e. against various types of anaemia.

Dialkylferrocenes (II)[48-51] and oxygen-containing[52,53] and sulphur-containing[54,55] ferrocenophanes of type (III) exhibit antianaemic activity:



(II)



(III)

; X=O or S .

The oxygen-containing compounds also exhibit a blood-liquefying activity.

The sodium salt of *o*-carboxybenzoylferrocene (ferrocerone)[56-60] is the first ferrocene-containing medicinal preparation whose widescale use in medical practice is permitted. Its characteristic features are non-toxicity,

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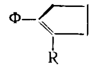
†This problem is discussed in detail in a monograph[30].

ready solubility in water, and rapid assimilation by the organism. Its application does not require the use of acids and it is therefore particularly suitable for administration to patients suffering from diseases of the gastro-intestinal system as well as children. It can be used in the treatment of various forms of anaemia and a severe disease of the nasopharynx—ozena, which hitherto has been virtually incurable.

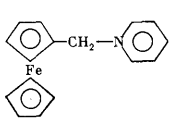
Substituted ferrocenylcyclopentenes have been proposed for the treatment of iron deficiency anaemia[61]:



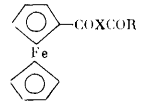
; R=Ph, $PhCH_2$, n-ClC_6H_4CO, or m-$CH_3C_6H_5CO$.

A complex medicine consisting of (1,1-diethyl-αα-thiobiscyclopentadienyl)iron and iron-dextran has been suggested recently[64]. It was found that the iron in this preparation, like that in ferrocerone[56-60], is absorbed in the liver.

Piperidinomethylferrocene exhibits a physiological activity[67]:

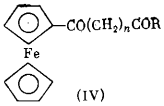


Ferrocene derivatives of the type



have been suggested for the treatment of disorders caused by iron deficiency in the organism. Here X is a saturated C_2–C_{10} hydrocarbon group and R is an alkyl group, a thiophen, furan, or benzene ring, or a benzene ring substituted by one or several halogen atoms or alkynyl groups.

Monoketones (IV), diketones (V), and hydroxyketones (VI) of the type[63]



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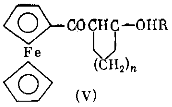
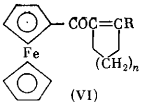


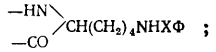
(V)



(VI)

have also been suggested[63].

Molecules of the type



$$\begin{matrix}—HN\diagdown \\ \diagup CH(CH_2)_4NHXΦ \\ —CO\end{matrix} ;$$

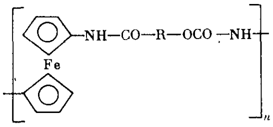
$X=CH_2$, CS—NH—CH_2, or $CO(CH_2)_2$.

based on ferrocenylacetic and ω-ferrocenylcaproic acids, have been obtained by grafting to the lysine residues in proteins[66]. Modified proteins of this type can be used in fluorescence microscopy; owing to their enhanced electron density, they are visible under the electron microscope.

Polymers obtained on the basis of ferrocenylenediacetic acid and diaminoferrocene can be used to study gas diffusion through membranes[67]:

;

R = $(CH_2)_4$, or $(CH_2)_6$



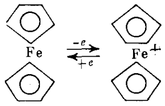
;

R = $(CH_2)_2$, $(CH_2)_4$, or $(CH_2)_6$.

They can also be used to study the following micro-organisms: *Candida pseudotropical*, *Mycobacteria BCG*, and *Mycobacterium foctuitum*. It has been noted[69] that compounds in which there is a possibility of ready elimination of a hydrogen halide showed the greatest bactericidal efficiency; there is a possibility of the formation of a double bond in the position conjugated to the CO group. It is striking that 3-chloropropionyl and 4-chlorobutyrylferrocenes are altogether ineffective.

VI. ION-EXCHANGE RESINS, REDOX SYSTEMS, SEMICONDUCTORS, AND INSULATORS

The use of ferrocene and its derivatives in various redox systems



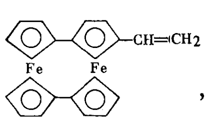
is based on their ability to undergo reversible oxidation to ferrocenium salts.

Electron-exchange resins based on ferrocene were first obtained by Nesmeyanov and coworkers[70,71]. A ferrocene electrode, ferrocene-containing polymers (redoxites), and liquid redox systems based on alkylferrocenes have been proposed[72-77]. Styrylferrocene–styrene copolymers exhibit electron-exchange properties[78]. Ion-exchange resins have been synthesised by grafting ferrocenyl residues (in the form of the amide of ferrocenedicarboxylic acid or formylferrocene) onto a fibre based on poly(vinyl alcohol)[81]. A biological redox system based on the reversible ferrocene–ferrocenium reaction at pH 7 has been used to convert cytochrome *c* into cytochrome *c* oxidase[80] and conversely.

Anion-exchange resins of a new type, based on cobaltocenium salts, have been suggested[81].

---o0o---

It has been shown that carefully purified polymers based on ferrocene do not exhibit paramagnetic properties[1,82,84]. Studies on partly oxidised ferrocene-containing polymers, which exhibit semiconducting properties, for example, polymers obtained from vinylferrocene and carbazole, constitute a new field in the chemistry of ferrocene[85]. Partial (to the extent of 60%) oxidation of the polymer obtained from vinylbis(fulvalene)iron



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gives rise to a product which has the highest specific magnetic susceptibility among the known organic semiconducting materials[86]. It appears that there is at present a possibility of employing ferrocene and its derivatives as organometallic semiconductors; investigators in a number of countries are carrying out vigorous researches in this field[84,87,88].

Detailed studies on the physicochemical properties of bis(fulvalene)iron and its mono- and di-cations yielded evidence that the monocation is a delocalised resonance-stabilised ion[89,90]—a representative of the so called mixed valence compounds. Thus the role of the ferrocene–ferrocenium system in the generation of semiconducting properties is evident.

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The study of partly oxidised ferrocene derivatives as semiconductors apparently stimulated research on the use of diamagnetic ferrocene compounds as insulators. Thus the addition of ferrocene (or its homologues) as well as polymers based on ketones and aldehydes derived from ferrocene to polyethylene increases the breakdown potential of the resulting dielectrics from 9.8 to 14.0 and 18.6 kV respectively[92]. An even more effective electrical insulator has been obtained from polyethylene, ferrocene, and isoprene GM.[93]

VII. FERROMAGNETIC MATERIALS BASED ON FERROCENE DECOMPOSITION PRODUCTS

On heating to 70–300°C with subsequent slow cooling to 25°C, ferrocene polymers[94] acquire ferromagnetic properties. Powders, solid materials, and thin shields made from these materials can be used in magnetic cores and in teleprinting and tele-reproducing devices and in magnetically shielded apparatus. The applications of organometallic compounds in electronics are described in greater detail in a monograph[95].

VIII. CHEMICAL REACTIONS INVOLVING METALLOCENES

1. Applications in Analytical Chemistry and in Methodological Chemical Research

Ferrocene has recently found increasing applications in analytical chemistry. The use of ferrocene in the potentiometric determination of molybdenum in metals, alloys, and steels[96] and the photometric determination of molybdenum in an aqueous organic medium[97] have been reported. The possibility of employing ferrocene in mixtures of glacial acetic and concentrated hydrochloric acids has been demonstrated in the direct amperometric oxidation-reduction titration of rhenium(VII) in aqueous organic media; many cations and anions do not interfere with the analysis[98].

Ferrocene has not become merely a generally accepted reagent of considerable importance in practice. Very recently it has come to be used as a methodological material for the training of students in procedures for the preparation of pure materials, the use of the infrared spectroscopic method in the determination of structure, in the gas–liquid chromatographic method, polarography, potentiometry, etc.[99]

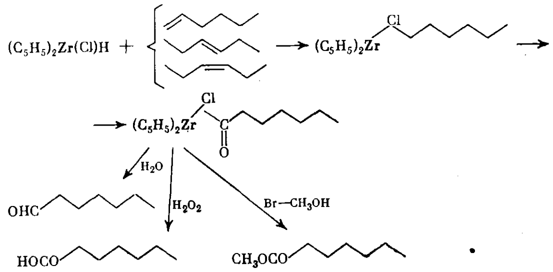
2. Catalysts of Chemical Processes

The oxidation of phenol by hydrogen peroxide in the presence of ferrocene or diacetylferrocene entails the formation of hydroquinone and catechol in proportions of 1 : 2.3 and in an almost quantitative yield[100]. Ferrocene–dichlorobenzene copolymers are capable of dehydrogenating and dehydrating alcohols[101].

When a solution of azulene is irradiated in the presence of sodium acetate and ferrocene in a carbon tetrachloride–ethanol mixture[102], the product is 1-ethoxycarbonylazulene. It has been noted that the irradiation of the same mixture in the absence of ferrocene or, conversely, in the presence of ferrocene derivatives with electron-donating (ethylferrocene) or electron-accepting (acetylferrocene) substituents does not yield satisfactory results.

Nickelocene $(C_5H_5Ni)_2$ catalyses many chemical processes. Thus a complex of the type $(C_5H_5)_2Ni.MX_n$ (where M = Al, Ti, or Nb; X = Cl; n = 3–5) polymerises butadiene with formation of polybutadiene containing *cis*-1,4-units[103,104]. Nickelocene in benzene or cyclohexane solution catalyses the hydrolysis of lignin to phenol[105]. The hydrolysis of lignin has become very important at the present time in connection with the problem of the elimination from the environment of the waste products of the cellulose industry. Reductive complex-formation reactions between phosphine sulphides and nickelocene have been described[106].

The hydrozirconation reactions in the presence of di(ηs-cyclo)pentadienyl(chloro)alkylzirconium hydride are being extensively investigated at the present time[107,108]. Carbon monoxide is inserted in the carbon–zirconium bond, olefins undergo oxidative hydrogenation, and, depending on the mode of the subsequent decomposition of the organozirconium compound, aldehydes, acids, or carboxylate esters may be obtained.



Cyclopentadienylzirconium(hafnium) dicarbonyls, $C_5H_5Zr(CO)_2$ and $C_5H_5Hf(CO)_2$, have been synthesised for the first time and tested as diphenylacetylene hydrogenation catalysts; their catalytic activity has been demonstrated. However, comparative analysis of the effect of equimolar amounts of these catalysts and cyclopentadienyltitanium dicarbonyl in the hydrogenation of phenylacetylene by hydrogen under a pressure of 3 atm showed that the latter is more effective[109].

Among organic derivatives of Group IV metals, mention should be made of dicyclopentadienyltitanium dichloride, which is widely used as a Ziegler–Natta catalyst in the polymerisation of ethylene and other mono- and poly-olefins[110,111]. Dicyclopentadienyltitanium dichloride in a 1 : 1 complex with triethylaluminium is also a hydrogenation catalyst: for example, it is used to convert oct-1-ene into n-octane[112]. The same complexes may be used as igniting agents for pyrotechnic compositions and as sources of free radicals[110].

The ability of dicyclopentadienyltitanium compounds to be reduced to compounds containing titanium in the lowest valence state, involving the intermediate formation of complexes with alkylaluminium halides, which ultimately leads to the appearance of free radicals, is believed[111] to be the main cause of the processes underlying the most important technological methods for the polymerisation of ethylene and other olefins.

Dicyclopentadienyltitanium dichloride also catalyses the fixation of molecular nitrogen[112-115]. Various systems are used in this process (for example $(\pi\text{-}C_5H_4)_2TiCl_2$, EtMgBr, $(\pi\text{-}C_5H_5)_2TiCl_2$, n-BuLi, etc.)

Vanadocene compounds proved to be active catalysts for the polymerisation of ethylene at room temperature[116]. The $(C_5H_5)_2VCl_2\text{–}CH_3AlCl_2$ and $C_5H_5VOCl_2\text{–}CH_3AlCl_2$ systems have been tested. In the first case polymerisation begins solely in the presence of oxygen as the initiator of chain transfer and termination. It has been suggested[116] that complexes of alkylated vanadium in the highest valence state are catalytically active.

An interesting report has been published recently concerning the use of cyclopentadienylcopper in the synthesis of acrylonitrile, methyl methacrylate, etc. polymers. The complex $C_5H_5Cu \leftarrow C{\equiv}N$-t-Bu is particularly effective in the polymerisation of acrylonitrile. The catalytic effect is appreciably enhanced in the presence of an excess (1 : 1) of t-BuCN and other ligands[117,118].

The use of cyclopentadienylmetal complexes in various chemical reactions constitutes a new rapidly developing field of homogeneous catalysis, which in the future may help us approach an understanding of the stereospecific processes occurring in the living organism at enormous rates at atmospheric pressure and at room or similar temperatures. The future applications of metallocenes will probably be found in this field, at the boundary between organic, organoelemental, and biological chemistry.

During the preparation of the manuscript for the press, a number of new reports were published on thermo- and photo-stabilisers[119-124], on photographic materials[125-131], on additives to fuels and oils[132-140], on medicinal substances[141-147], on semiconductors and insulators[148-154], on ferromagnetic materials[155], on applications in analytical chemistry[156-163], and on catalysts of chemical processes[164,165].

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The Hydroperoxy-radical ($H\dot{O}_2$) in V.V.Voevodskii's Research and at the Present Time. Results and Problems

V.L.Tal'roze and A.I.Poroikova

The role of $H\dot{O}_2$ radicals in the kinetics of the gas-phase oxidation of hydrogen-containing substances is considered. It is shown that at a high concentration of active centres, for example, when the latter are generated under the influence of a fairly powerful radiation source, non-linear reactions of $H\dot{O}_2$ radicals, i.e. their interaction with one another and with other active species, become important. These processes play an important role in the following kinetic systems considered: at the second limit in mixtures of hydrogen with oxygen under the conditions of artificial chain initiation; in the region of Earth's ozone layer; in lasers based on the reactions between H_2 and F_2.
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I. INTRODUCTION

The ways of science are strange and unpredictable. Two different and sometimes opposite pathways converge unexpectedly. Similarly human beings following such pathways (if still alive) may meet or their memories may be juxtaposed and it would seem that everything could be predicted if one thought on these lines. This rare gift of prediction was to a large extent typical of Vladislav Vladislavovich Voevodskii.

Returning periodically to the study of $H\dot{O}_2$ radicals, mainly after Voevodskii's death, we realised how much Voevodskii foresaw in those cases where others saw only exercises in the solution of kinetic equations. Thirty years ago, at the time when one of the present authors was Voevodskii's Diploma Student, Voevodskii stated: "in this triatomic species ($H\dot{O}_2$ radical) are contained half of the future oxidation theories; it is a live radical, which is destroyed on the walls only in narrow tubes, and in all real instances it behaves as a truly reactive substance like hydrogen and oxygen atoms. If we learn to measure $H\dot{O}_2$ radicals, we shall obtain a key to oxidation mechanisms".

Thirty years have elapsed and these ideas, confirmed by extensive experimental data, have become generally accepted in the chemistry of the gas-phase oxidation of hydrogen-containing substances. It is now well known that $H\dot{O}_2$ radicals are formed in the oxidation of hydrogen, hydrocarbons, aldehydes, alcohols, ketones, ethers, and many other hydrogen-containing organic and inorganic substances.

The first hypothesis of the formation of $H\dot{O}_2$ in the gas phase was put forward in 1926 by Marshall[1] and independently by Taylor[2] in order to explain the results obtained in the oxidation of hydrogen photosensitised by mercury. The rate constant for the formation of $H\dot{O}_2$ radicals

$$\dot{H} + O_2 + M \rightarrow H\dot{O}_2 + M \tag{1}$$

was estimated in 1930[3] and at the same time Hinshelwood explained the second self-ignition limit in hydrogen-oxygen mixtures by chain termination in terms of reaction (1).[3,4] The $H\dot{O}_2$ radical appeared for the first time in 1937 in hypothetical hydrocarbon oxidation mechanisms when von Elbe and Lewis published a radical-chain mechanism for the oxidation of paraffinic hydrocarbons[5]. At the end of the 1940s, Voevodskii attempted to detect $H\dot{O}_2$ radicals on the basis of the gases evolved by frozen products in the study of the oxidation of hydrogen above the second limit. This investigation initiated a series of others, where the rate constant for the chain branching reaction was measured:

$$\dot{H} + O_2 \rightarrow \dot{O}H + \dot{O} \tag{2}$$

and the relative efficiency of the water molecules in reaction (1) was estimated[6,7]. The ratio $k_1^{H_2O}/k_1^{H_2} = 5$ obtained[6] still remains virtually unchanged.

The study of the oxidation of hydrogen at atmospheric pressure near the third limit in reactors treated with acids[7,8] led Voevodskii to the conclusion that at an early stage of the process hydrogen peroxide is the main product, in agreement with Kondrat'ev's preliminary data[9]. This feature of the oxidation of hydrogen in acid-treated reactors indicated the importance of the formation of hydrogen peroxide

$$2H\dot{O}_2 \rightarrow H_2O_2 + O_2 \tag{3}$$

together with the process

$$H\dot{O}_2 + H_2 \rightarrow H_2O_2 + \dot{H}\,. \tag{4}$$

(In the subsequent decades this idea was developed by Baldwin[10,11] and others.)

The measurement of the rate constant for reaction (4) is difficult because of the low rate of this process. In the study of the oxidation of hydrogen above the second limit Voevodskii was able to measure k_4,[6,7] which, together with the few available data obtained by other workers, served as a basis for the value recommended by Baulch[12].

Even when he became attracted to many new problems, Voevodskii continued to be interested in the reactions of $H\dot{O}_2$ radicals. Seventeen years after the first attempt to detect $H\dot{O}_2$, Panfilov, one of Voevodskii's students, successfully applied the EPR method to the determination of frozen $H\dot{O}_2$ radicals in hydrogen combustion products[13]. Soon afterwards, Nalbandyan and coworkers[14] converted the radical "freezing out" method with subsequent analysis of the EPR spectra into a quantitative procedure for the determination of $H\dot{O}_2$ and $R\dot{O}_2$ radicals in gas-phase oxidation and combustion reactions.

The regions corresponding to the combustion and slow oxidation of hydrogen were reinvestigated in order to study the characteristics of the accumulation of $H\dot{O}_2$ radicals. In particular, it was shown[14] that, in the region of the slow reaction between the second and third limits, the $H\dot{O}_2$ concentration is 10^{13} radical cm^{-3} and increases as the third limit is approached[14,15], as predicted by Voevodskii's calculations[7].

Using a modified method involving the freezing out of $H\dot{O}_2$ and $R\dot{O}_2$ radicals (fractionation) and analysing their EPR spectra, Nalbandyan and Mantashyan[14] established that the oxidation of hydrocarbons and lower aldehydes also involve the formation of $H\dot{O}_2$ radicals at a high concentration. The following processes serve as the sources of these active species:

$$\dot{C}_nH_{2n+1} + O_2 \rightarrow [\dot{C}_nH_{2n}O_2H] \rightarrow H\dot{O}_2 + C_nH_{2n},$$

$$\dot{C}_nH_{2n+1} + O_2 \rightarrow H\dot{O}_2 + C_nH_{2n},$$

$$H\dot{C}O\ (\text{from aldehydes}) + O_2 \rightarrow H\dot{O}_2 + CO,$$

$$CO + \dot{O}H \rightarrow CO_2 + \dot{H} \xrightarrow{+O_2+M} H\dot{O}_2 .$$

On passing from the low-temperature to the higher-temperature region in the oxidation of hydrocarbons[5], the ratio $[H\dot{O}_2]/[R\dot{O}_2]$ increases appreciably[14]. This finding confirms the earlier hypothesis concerning the change in the mechanism of the oxidation of hydrocarbon on passing through the region corresponding to a negative temperature coefficient of the reaction and the involvement of $H\dot{O}_2$ radicals in chain propagation reactions in the higher-temperature oxidation region[14].

Whereas in the low-temperature oxidation region the formation of $H\dot{O}_2$ radicals leads to chain termination, on raising the temperature chain propagation reactions become important:

$$H\dot{O}_2 + RH \rightarrow H_2O_2 + \dot{R}, \qquad (5)$$

$$H\dot{O}_2 + R'CHO \rightarrow H_2O_2 + R'\dot{C}O, \qquad (6)$$

and the decomposition of the hydrogen peroxide formed leads to degenerate branching. Thus it was found that, in agreement with Voevodskii's views, in the higher-temperature oxidation region the $H\dot{O}_2$ radical is an active intermediate—a chain carrier.

For a quantitative description of the oxidation of hydrocarbons at a high temperature, it is necessary to know the rate constants for reactions (5) and (6), the few available values for which are listed in Table 1. The rate constants for the interaction of $H\dot{O}_2$ radicals with paraffinic hydrocarbons, presented in Lloyd's review[3], were measured by Baldwin and coworkers at a single temperature (500°C). Assuming that the activation energy for C_2H_6 is 14 kcal $mole^{-1}$ and that the difference between the enthalpies of reaction (5) enters into the activation energy with a coefficient of unity (according to the Semenov–Polanyi rule, with a coefficient of 0.75 for endothermic reactions[17]), Lloyd[3] obtained the Arrhenius parameters of reactions (5) listed in Table 1.

The products of the interaction of $H\dot{O}_2$ radicals with olefins are unknown[3,18]. The rate constants have been estimated[18].

We examined the pathways followed in the "linear" reactions of $H\dot{O}_2$ in the oxidation of hydrogen and hydrocarbons, i.e. the reactions of $H\dot{O}_2$ radicals with stable substances. These processes are important, because they lead to the third chain limit in the oxidation of hydrogen[7] and to the characteristics of the higher-temperature oxidation of hydrocarbons mentioned above.

However, nowadays non-linear reactions of $H\dot{O}_2$ radicals and their reactions with active species are attracting the attention of investigators to an increasing extent. We shall demonstrate three examples of the importance of non-linear processes involving $H\dot{O}_2$ radicals. We shall consider only situations in which the initial reactions where the species are generated are associated with the effect of radiation on reactive gaseous mixtures: (1) the influence of modern sources of ionising radiation (isotopes, nuclear reactors, accelerators) on the ignition limits associated with a branched chain mechanism; (2) the reactions of $H\dot{O}_2$ radicals in Earth's ozonosphere; (3) the reactions of $H\dot{O}_2$ radicals in common chemical lasers. As classical examples, we shall consider a mixture of hydrogen and oxygen for the first case and the working mixture in the laser whose operation is based on the reaction between H_2 and F_2 (the mechanism of this reaction was discovered at the Institute of Chemical Physics[19,20] and the most important chemical lasers in existence at the present time are based on it) for the third case.

Table 1. The rate constants for reactions (5) and (6) $[k = A\exp(-E/RT)]$.

RH	C_2H_6	C_3H_8	n-C_4H_{10}	iso-C_4H_{10}	CH_2O*
ΔH_i, kcal $mole^{-1}$	8.36	4.84	4.97	1.27	—0.9
E, kcal $mole^{-1}$	14.0	10.5	10.5	7.0	10.4
lg A (cm^3 $mole^{-1}$ s^{-1})	12.0	11.3	11.7	11.0	13.0

*k was measured in the temperature range 773–793 K [16]; for the remaining RH, estimates taken from Ref. 3 are quoted.

II. NON-LINEAR REACTIONS OF $H\dot{O}_2$ RADICALS ASSOCIATED WITH THE OXIDATION OF HYDROGEN

The problem of the influence of radiation and of other physical methods for the generation of active species on the reaction of hydrogen with oxygen is the problem of the positive interaction of chains. The idea, logic, and initial method are due to Semenov[17] and the first postwar experiments, on the basis of which Semenov derived the mechanism, were carried out by Dubovitskii and Nalbandyan[21]. According to Semenov's calculation[17], when one begins with the rate of generation of oxygen atoms in Nalbandyan's photochemical experiments and one assumes that $H\dot{O}_2$ radicals are destroyed on the reactor wall and the chains interact solely via the reaction

$$\dot{H} + H\dot{O}_2 \rightarrow 2\dot{O}H,$$

then a rate constant of 10^{-11} cm^2 $molecule^{-1}$ s^{-1} must be attributed to the latter reaction in order to account for the observed limiting increase of pressure. Since that time the reaction between $\dot{H}$ and $H\dot{O}_2$, which was found to proceed via the three channels

$$\dot{H}+H\dot{O}_2 \begin{cases} \longrightarrow 2\dot{O}H, & (7) \\ \longrightarrow H_2+O_2, & (8) \\ \longrightarrow H_2O+\ddot{O}, & (9) \end{cases}$$

has been the subject of numerous investigations. Table 2 presents the experimental data accumulated hitherto. If Westenberg's results (which are probably erroneous[22,31]) are rejected, then, despite the quantitative discrepancy, all these data confirm a single main idea: the reaction between $\dot{H}$ and $H\dot{O}_2$ involves chain branching and not chain termination, in agreement with Semenov's hypothesis, because $k_8 < k_7 + k_9$.

Table 2. The ratios of the rate constants for the chain termination and propagation channels in the reaction between $\dot{H}$ and $H\dot{O}_2$.

T, K	$\frac{k_8}{k_7+k_9}$	Method	Refs.
773	0.17	Computer calculation, IInd limit in $H_2 + O_2$ reaction	22
900	0.15	Rate of $H_2 + O_2 + N_2$ flame propagation, computer calculation	23—25
293	0.50	Extrapolation of high-temperature data	23—25
291	0.51±0.2	Discharge flow, measurement of H and H_2O concentrations; $p = 2$ mmHg	26
291	0.75±0.25	Discharge flow, EPR; $p = 50–250$ mmHg	27
291	0.76	Diffusion cloud, mass spectrometry; $p = 20$ mmHg	28
291	1.6	Discharge flow, EPR; $p \leqslant 2.5$ mmHg	29
293	0.41	Discharge flow, EPR; $p = 10$ mmHg	30

As a result of the studies by Baldwin[11] and other investigators[32], it is known that the mechanism of the oxidation of hydrogen at the second ignition limit depends to a large extent on the treatment of the reaction vessel walls. In vessels treated with oxides and certain metal chlorides the active centres are destroyed at a higher rate on the reactor surface. The principal characteristics observed at the first and second ignition limits can then be accounted for in terms of a reaction mechanism involving only linear reaction processes:

$$H_2+O_2 \rightarrow 2\dot{O}H, \qquad (10)$$

$$\dot{O}H+H_2 \rightarrow H_2O+\dot{H}, \qquad (11)$$

$$\dot{H}+O_2 \rightarrow \dot{O}H+\ddot{O}, \qquad (2)$$

$$\ddot{O}+H_2 \rightarrow \dot{O}H+\dot{H}, \qquad (12)$$

$$\dot{H} \xrightarrow{\text{wall}} (H)_w,$$

$$\ddot{O} \xrightarrow{\text{wall}} (O)_w,$$

$$\dot{O}H \xrightarrow{\text{wall}} (OH)_w,$$

$$\dot{H}+O_2+M \rightarrow H\dot{O}_2+M, \qquad (1)$$

$$H\dot{O}_2 \xrightarrow{\text{wall}} (HO_2)_w.$$

The opposite case of the "fully reflecting" surface is that of the surface of reactors treated with acids[32] and primarily with boric acid[10,11]. Here the probability of the destruction of $H\dot{O}_2$ radicals on the wall is low ($\leqslant 10^{-4}$)[33] and the non-linear processes (7)–(9) and (3) make a considerable contribution to the mechanism of the oxidation of hydrogen near the second limit. Experiments show that in acid-treated vessels the second limit occurs at a higher pressure, which also indicates the dominance of the positive chain interaction processes (7) and (9).

The problem of the possible influence of ionising radiation on the ignition region has been examined[34]. After the essential features of the interaction of ions with molecules were established a quarter of a century ago and the corresponding rate constants were estimated, it became possible to convert the fluxed and doses of ionising radiation into the absolute rates of initiation of chemical reactions by such radiation[35]. The *EFDC* plot of the logarithm of the radiation dose rate against the reciprocal of temperature in Fig. 1, taken from Tal'roze[34], shows the dose rates for which the effect of radiation is significant. The region of an appreciable effect by the radiation is limited by plots corresponding to the following four criteria proposed for the analysis of the problem of the radiation-induced initiation of chain processes[34].

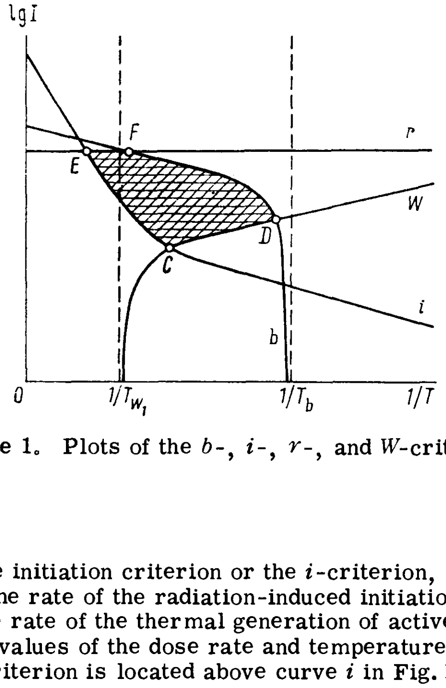

Figure 1. Plots of the b-, i-, r-, and W-criteria.

1. The initiation criterion or the i-criterion, according to which the rate of the radiation-induced initiation must exceed the rate of the thermal generation of active centres; the set of values of the dose rate and temperature satisfying this criterion is located above curve i in Fig. 1.
2. The branching criterion or b-criterion, requiring that the reaction should be self-accelerating under isothermal conditions. This characteristic of the process should be observed to the left of curve b.
3. The absolute rate or W-criterion, according to which it is necessary that the overall reaction rates should exceed a value selected on the grounds of practical considerations. This criterion is satisfied to the right of curve W.
4. The criterion concerning the presence of a source of sufficient intensity or the r-criterion. It is satisfied below the horizontal straight line r corresponding to the maximum dose rate which may be established in the reaction mixture using a particular type of ionising radiation source.

On the basis of the plots in Fig. 1, one may expect that radiation affects the ignition limits for a hydrogen–oxygen mixture only in the range of dose rates corresponding to the region *EFDC*. The calculations of Poroikova et al.[36] do indeed show that the ionising radiation from the available sources can alter the position of the second ignition limit in hydrogen–oxygen mixtures.

Fig. 2 presents the results of calculations in terms of plots of the dimensionless pressure at the second limit against the logarithm of the ratio of the rate of artificial initiation and the rate of thermal chain generation [the calculation was performed for the following conditions: stoichiometric mixture, 723 K, cylindrical vessel with a radius of 2 cm, and the ratio $k_8/(k_7 + k_9) = 0.15$]. The limit is appreciably displaced when the rate of artificial initiation corresponds to a dose rate of 10^{14}–10^{17} eV cm^{-3} s^{-1}, which requires the use of powerful radiation sources.

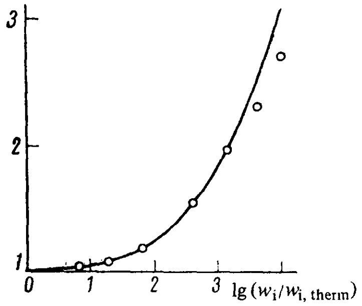

Figure 2. Dependence of the pressure at the second limit on the rate of artificial initiation; p_{II}—pressure at the limit; $p_{II, therm}$—pressure at the limit corresponding to thermal chain initiation; W_i—rate of artificial initiation; $W_{i, therm}$—rate of thermal generation of active centres.

The circles in Fig. 2 present the results of the calculation by the equation obtained for the second limit taking into account reactions (1)–(4) and (7)–(12), while the continuous line represents the results of the calculation of the second limit on a computer taking into account a more complex mechanism, including the consumption of the initial substances, the self-heating of the reacting mixture, the formation and consumption of hydrogen peroxide, and a number of other non-linear processes[33,36].

Evidently the results of the two calculations agree over a wide range of artificial initiation rates. The limit is controlled by processes (1) and (2) (as for a linear mechanism) and by the quadratic reactions (3) and (7) to (9). At higher rates of initiation there is an additional displacement of the limit (the continuous line passes above the circles) owing to the self-heating of the mixture[33,36].

Thus the four non-linear processes (3) and (7)–(9) involving $H\dot{O}_2$ radicals determine the position of the thermal limit in acid-treated vessels and the displacement of the limit following artificial chain initiation. In order to calculate the limit, it is necessary to know both the overall rate constant for the reaction between H and $H\dot{O}_2$ and the ratio of the rate constants for the chain propagation and termination channels and their temperature dependence. Values of the above ratio obtained by various workers are listed in Table 2. All the low-temperature results refer to the system where H atoms were obtained from a discharge and the overall pressure in the reaction vessel was several mmHg. In his analysis of causes of the discrepancies between the results, Lloyd[3] points to the possible contribution of excited $H\dot{O}_2^*$ species to the reaction with H atoms [the heat of reaction (1) is 47 kcal mole^{-1}]. It has been shown[37] that an even more important source of errors is the formation in the discharge of excited hydrogen molecules whose interaction with $\dot{O}H$ radicals takes place with a low activation energy. The corresponding increase in the concentration of $\dot{H}$ atoms and the decrease in the concentration of $\dot{O}H$ radicals may lead[37] to unduly low values of k_7 and of the overall rate constant for the reaction between $\dot{H}$ and $H\dot{O}_2$ (in the available data[22–30], the values of the overall rate constant vary by a factor of 3).

The high temperature results, quoted by Baldwin et al.[22] and by Dixon-Lewis and coworkers[23–25] for only one temperature, were obtained by comparing the experimental position of the second limit and the rate of propagation of the hydrogen-oxygen flame with a very complex oxidation mechanism. The values obtained are thus based on certain numerical rate constants for a whole series of other processes. The rate constants for reactions (7)–(9) and the corresponding activation energies quoted by Hampson and Garvin[38] must therefore be regarded as estimates.

The rate constant for reaction (3) has been measured by many investigators[12]. The activation energy for this process is unknown but is probably small[3]. According to Lloyd's estimates[3], k_3 at 700–800 K is known within the limits of a factor of 2.

It follows from the foregoing data that reliable measurements of the rates of reactions (3) and (7)–(9) are necessary over a wide temperature range.

III. REACTIONS OF $H\dot{O}_2$ RADICALS IN EARTH'S OZONOSPHERE

Earth's ozonosphere is a giant photochemical reactor in the ultraviolet part of the spectrum. Until recently it was believed that the photochemistry of the ozone layer is limited to Chapman's oxygen cycle[38]:

$$O_2 + h\nu \rightarrow 2\ddot{O}, \tag{13}$$

$$\ddot{O} + O_2 + M \rightarrow O_3 + M, \tag{14}$$

$$O_3 + h\nu \rightarrow \ddot{O} + O_2, \tag{15}$$

$$\ddot{O} + O_3 \rightarrow 2O_2, \tag{16}$$

in which reactions (14) and (15) are rapid. Reaction (13) involves the generation of active substances comprising the so called odd oxygen (oxygen atoms and ozone molecules), while reaction (16) involves their destruction.

At least three more groups of chain reactions opposing the tendency of sunlight to generate odd oxygen, are known at the present time. These groups are the hydrogen, nitrogen, and chlorine ozone decomposition cycles. The reactions in these cycles, together with processes (13) and (16) control the steady-state concentration of ozone (in the ozone layer the concentration of oxygen atoms is much smaller than the concentration of ozone).

The active species in the hydrogen cycle, the so called odd hydrogen ($\dot{H}$ atoms, $\dot{O}H$ and $H\dot{O}_2$ radicals, and H_2O_2 molecules), are formed from the H_2O, H_2, and CH_4

molecules arriving from Earth's surface. The most important processes in the hydrogen cycle are the following reactions in which the $\dot{O}H$ and $H\dot{O}_2$ radicals behave as catalysts of the decomposition of odd oxygen:

$$\begin{aligned} O_3 + \dot{O}H &\rightarrow H\dot{O}_2 + O_2\ , \\ H\dot{O}_2 + \ddot{O} &\rightarrow \dot{O}H + O_2\ , \\ O_3 + H\dot{O}_2 &\rightarrow \dot{O}H + 2O_2\ , \\ \dot{O}H + \ddot{O} &\rightarrow \dot{H} + O_2\ , \\ \dot{H} + O_2 + M &\rightarrow H\dot{O}_2 + M\ . \end{aligned}$$

These processes involve the termination of odd oxygen chains, while in relation to the substances constituting odd hydrogen they are chain propagation reactions (the interaction of the hydrogen and oxygen cycles).

Examples of other important chain propagation reactions are presented below:

$$\begin{aligned} 2H\dot{O}_2 &\rightarrow H_2O_2 + O_2, \\ H_2O_2 + h\nu &\rightarrow 2\dot{O}H, \\ H\dot{O}_2 + NO &\rightarrow \dot{O}H + NO_2, \\ H\dot{O}_2 + CH_3\dot{O}_2 &\rightarrow CH_3O_2H + O_2, \\ CH_3O_2H + h\nu &\rightarrow CH_3\dot{O} + \dot{O}H. \end{aligned} \tag{17}$$

Here Eqn. (17) represents the interaction of the hydrogen and nitrogen cycles (the substances constituting odd nitrogen are NO, NO_2, NO_3, N_2O_5, HNO_3, and HNO_2). The last two processes are associated with the oxidation of natural methane.

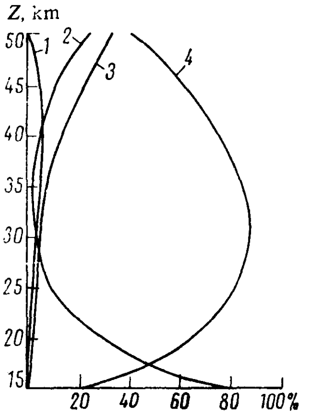

Figure 3. Contribution of the cycles to the rate of decomposition of ozone (%): 1) ClO_X; 2) HO_X; 3) O_X; 4) NO_X.

The relative contribution of the hydrogen cycle to the decomposition of ozone and the relative roles of other ozone decomposition cycles, which we recently calculated[39], are presented in Fig. 3. Evidently the chain reaction involving $H\dot{O}_2$ makes different contributions to the decomposition of ozone and in the lower ozonosphere this contribution may reach 2/3. We chose the chain length ν, equal to the number of odd oxygen molecules decomposed by one molecule of the cycle catalyst, as a measure of the efficiency of cycles in the decomposition of odd oxygen. The ozone decomposition chain length in each cycle, calculated by Tal'roze et al.[39], is presented in Fig. 4. Evidently the chain length in the hydrogen cycle has the smallest dependence on the height above sea level (Z) and amounts on average to several hundreds of units.

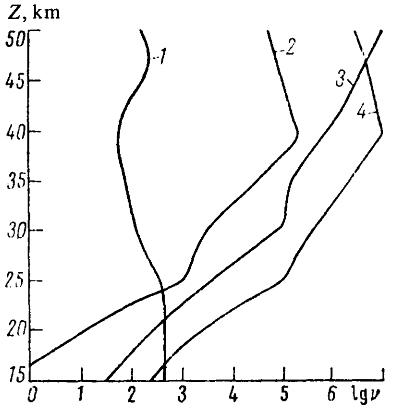

Figure 4. Odd oxygen chain lengths in different cycles: 1) HO_X; 2) ClO_X; 3) NO_X; 4) BrO_X.

Thus the key position of $H\dot{O}_2$ in the chemistry of the ozonosphere is determined to a large extent by its involvement in the "mixing" of different groups of chemical reactions, i.e. in non-linear interactions with active species of other cycles. Apart from the chain propagation reactions described above, the following interactions between the cycles are important:

$$\left.\begin{array}{l} H\dot{O}_2 + \dot{O}H \rightarrow O_2 + H_2O \\ H\dot{O}_2 + NO_2 \rightarrow O_2 + HNO_2 \\ H\dot{O}_2 + NO + M \rightarrow M + HNO_3 \\ H\dot{O}_2 + \dot{C}l \rightarrow O_2 + HCl \\ \\ H\dot{O}_2 + CH_3\dot{O} \rightarrow O_2 + CH_3OH \end{array}\right\} \begin{array}{l} \text{(chain termination in the } HO_X \text{ cycle)} \\ \text{transfer, washing out by rain } \rightarrow \\ \rightarrow \text{termination in both cycles} \\ \xrightarrow{+\dot{O}H} H_2O + NO_x, ClO_x \text{ (partial termination} \\ \text{in } HO_X \text{ cycle)} \\ \xrightarrow{+h\nu} \text{ regeneration of cycles} \end{array}$$

These processes largely lead to chain termination, but there also exists a chain propagation channel (photochemical decomposition).

Chain termination in the nitrogen and chlorine cycles takes place via the diffusion of acid species (HNO_X and HCl) to the troposphere and their subsequent washing out by rain. The rate of this process may be calculated with the aid of vertical turbulent diffusion coefficients, which have been estimated by many workers[39-41]. Compared with the rate of transfer, the chemical chain termination reaction

$$H\dot{O}_2 + \dot{O}H \rightarrow O_2 + H_2O \tag{18}$$

takes place at a high rate in the stratosphere. This explains the relatively small length of the ozone decomposition chain in the hydrogen cycle. Thus reaction (18) is one of the key elementary processes influencing ozone in the lower stratosphere. Many investigators have been devoted to the measurement of the rate constant for reaction (17). Its reliable measurements are difficult in view of the complexity of the systems in which $\dot{O}H$ and $H\dot{O}_2$ radicals may be obtained simultaneously. Hampson and Garvin[38] recommend values of k_{17} in the range from 2×10^{-11} to 2×10^{-10} cm^{-3} mol.$^{-1}$ s^{-1}, but the scatter of the literature data exceeds this range.

IV. THE $H\dot{O}_2$ RADICAL IN THE LASER BASED ON THE REACTION BETWEEN H_2 AND F_2†

The emission from these lasers is in the infrared because the elementary reactions

$$\dot{H} + F_2 \rightarrow HF + \dot{F},$$
$$\dot{F} + H_2 \rightarrow HF + \dot{H}$$

lead to the generation of inverted populations of vibrationally excited HF molecules. Despite the outward simplicity of the system, it is difficult to control the active process in the chemical laser. In the first place, when one is dealing with pulsed lasers, it is necessary to mix the initial substances under a considerable pressure. Shilov, Chaikin, and coworkers[19,20] found a simple solution to this problem: oxygen is added and the stabilisation process, which produces a second ignition limit in the fluorine–hydrogen mixture under the conditions of vigorous branching, is

$$\dot{H} + O_2 + M \rightarrow H\dot{O}_2 + M. \qquad (1)$$

The question arises of the subsequent fate of the $H\dot{O}_2$ radicals and whether or not it is important. This problem has been inadequately analysed and we shall point to only one of its aspects.

A pulsed chemical laser operates effectively under the conditions of intense initiation of the chain reaction. The initiation is achieved by some kind of influence on the fluorine–hydrogen mixture which leads to the appearance of fluorine atoms. The intensity of the initiation is usually such that, after a short period, the concentration of fluorine atoms reaches 0.1–1% of the initial concentration of molecules. It is noteworthy that, in a mixture having a nearly stoichiometric composition, the "slow" active centre is the hydrogen atom and the number of hydrogen atoms is virtually equal to the number of generated fluorine atoms. This factor distinguishes significantly the conditions in the pulsed reaction between fluorine and hydrogen from those in the thermal reaction and also from the reaction between hydrogen and oxygen in the initial stages of self-ignition. Indeed the $H\dot{O}_2$ radicals formed can no longer be regarded as relatively inactive, because the mixture contains a substance (hydrogen atoms) the concentration of which is sufficient to react rapidly with $H\dot{O}_2$ radicals. The hydroxy-radicals formed in this process can react with molecular hydrogen to generate hydrogen atoms. The rate constant for this reaction can be in principle very large and close to the collision number, since the $\dot{O}H$ radicals formed have an average excitation energy of 20 kcal mole^{-1}. Thus the situation of "an infinite chain length" is created.

Such are the three kinetic systems, outwardly so different and yet identical as regards the important role of $H\dot{O}_2$ radicals, to the understanding of which Voevodskii's fundamental ideas have made a significant contribution.

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†For the description of chemical lasers employing the reaction between H_2 and F_2, see Refs. 42–44.

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Infrared Photochemistry

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The characteristics of chemical reactions under the influence of infrared radiation and the conditions under which they occur in the absence of equilibrium between the vibrational and other degrees of freedom of the reacting species are examined. Studies on isotopically selective reactions, on the role of various types of energy (namely vibrational and translational energy), and on the overcoming of the activation barrier in chemical reactions are analysed.
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I. INTRODUCTION

The vigorous development of laser techniques in recent years has greatly extended the scope of photochemistry. The application of lasers with ultrashort (picoseconds) pulses made it possible to investigate ultrafast processes which previously had not been susceptible to direct experimental investigation. High radiation densities (megawatts and gigawatts per square centimetre) made it possible to achieve readily multiquantum processes. The highly monochromatic nature of laser radiation has led to selective photochemical reactions (including reactions selective with respect to isotopes).

Whereas in the visible and ultraviolet regions (i.e. in the regions of electronic transitions) the appearance of lasers significantly extended the scope of photochemistry, in the infrared region (i.e. in the region of vibrational transitions) photochemical research has become in general possible only after lasers became available. Until then there had been no sources of infrared radiation with a sufficiently high intensity to be capable of generating in a single, not necessarily very narrow, part of the spectrum excited species at a higher rate than in thermal equilibration processes. Infrared spectroscopy existed but not infrared photochemistry. One can point to only one study of the pre-laser period[1] whose author investigated the *cis*–*trans* isomerisation of nitrous acid in a low-temperature matrix (at 20 K) under the influence of infrared radiation isolated by filters from the emission spectrum of a heated body.

Numerous studies have now been published on infrared laser photochemistry. Some of them have been analysed in review articles on the chemical action of laser emissions[2-16] and the laser method for isotope separation[17-21] as well as a number of popular articles[22-25]. Most of the reviews have dealt with processes occurring under the influence of laser radiation over the entire spectral range and comparatively little attention has been devoted to the infrared region. Only brief reviews have been devoted to problems of infrared laser photochemistry[5,13].

We shall now formulate the fundamental distinctive features of infrared photochemistry, i.e. the photochemistry of vibrationally excited molecules, in relation to the photochemistry in the ultraviolet and visible regions, i.e. the photochemistry of electronically excited states.

The primary step in photochemical processes under the influence of ultraviolet and visible radiation is the formation of electronically excited species, which then usually decompose or isomerise. The large electronic excitation quanta make the contribution of the thermal reaction pathway insignificant compared with the photochemical pathway. When an infrared quantum is absorbed, vibrationally excited species are formed in the ground electronic state. Owing to the smallness of the infrared quanta, the population of the corresponding vibrationally excited state corresponding to thermal equilibrium is not as a rule negligibly small compared with the population induced by the radiation. For this reason, one of the distinctive features of infrared photochemistry is methodological difficulties associated with the competition between the photochemical and thermal reaction pathways. These difficulties are eliminated mainly by reducing the pressure and temperature. A decrease of pressure retards the deactivation of excited molecules, which is determined by vibrational relaxation in collisions with other species, while a decrease of temperature diminishes the thermal population of the vibrationally excited states. Thus infrared photochemistry is mainly the photochemistry of low pressures and temperatures.

Chemical reactions under the influence of ultraviolet and visible radiation are determined as a rule by the reactivity of the excited state formed in the primary light absorption step. In the infrared region this situation is rarely encountered. It is prevented by intramolecular vibrational energy transfer between different vibrational degrees of freedom, which is very rapid in complex molecules. For this reason, chemical reactions under the influence of infrared radiation may be determined by the reactivity of not only the directly excited bond but also of others. Furthermore, in the infrared region intermolecular energy transfer also plays a relatively major role. As a result, other more reactive species react instead of the molecule excited by infrared radiation; thus infrared photosensitisation must be a fairly common phenomenon.

One of the characteristics of infrared photochemistry is associated with the fact that the reactivity of vibrationally excited molecules increases sharply with increase in the amount of vibrational energy. For a fairly large amount of energy, other processes, such as the dissociation and ionisation of the molecule, also become possible. Multiquantum processes, i.e. processes involving highly excited states, therefore play an extremely important role in the infrared region.

Finally we may note that in the infrared region the quantum yields are usually low, whereas in electronic excitation they frequently approach unity. This is associated primarily with the relatively high rates of deactivation processes compared with the rate of reaction. On the other hand the faster multiquantum processes, such as multiquantum dissociation processes, show quantum yields much less than unity by virtue of the very nature of the process.

In the light of the characteristics of infrared photochemistry formulated above, one may specify three types of chemical reactions, with different degrees of complexity, under the influence of infrared radiation. Firstly, these are reactions under conditions where there is no equilibrium between the vibrational and translational degrees of freedom. One of the main scientific problems in these investigations involves the study of chemical reactions under non-equilibrium conditions, which is very important not only for laser photochemistry but also for plasma chemistry, chemical combustion, and other problems of practical importance. Whereas it is evident that in unimolecular decomposition reactions the vibrational energy is in fact responsible for overcoming the activation barrier, in bimolecular and other reactions the problem is more complex. One of the tasks in infrared laser photochemistry is the elucidation of the role of various types of energy (particularly vibrational energy) in the overcoming of the activation barrier in chemical reactions. A practical aspect of the studies under consideration is a more economical utilisation of the energy required to carry out the chemical reactions. In this case the energy is consumed in "heating" only the vibrational degrees of freedom of the reacting species and not of the entire substance. The high efficiency of modern infrared lasers (particularly the CO_2 laser) permits one to hope that they may be used in practice to achieve processes of this kind.

The second task—the selective involvement in the reaction of molecules having similar chemical properties, particularly isotopic molecules—is more complex. The high rates of exchange of vibrational energy between them make it possible to carry out such processes only in gases at low pressures or in the condensed phase at low temperatures under the conditions of matrix isolation of the excited molecules. Still greater difficulties arise in the solution of the third problem—the achievement of reactions via a selected pathway by "exciting" the corresponding vibrations as a result of the absorption of infrared radiation. Rapid intramolecular transfer of vibrational energy between different degrees of freedom in complex molecules prevents this.

Most studies on infrared laser photochemistry refer to processes in gases at low pressures. They can be divided into two groups. The first involves the study of the dissociation of polyatomic molecules as a result of multiphoton excitation by the action of powerful and short radiation pulses of infrared lasers (particularly the CO_2 laser) and the second involves the study of reactions with atoms and free radicals of molecules whose degree of vibrational excitation is comparatively low. Furthermore, there have been numerous studies where chemical reactions under the influence of infrared laser radiation were due to equilibrium thermal heating. These are mainly processes in gases at comparatively high pressures (tens and hundreds of mmHg) under the influence of continuous laser radiation. The number of studies on chemical reactions in the condensed phase or on solid surfaces has been much smaller owing to the high rates of relaxation of vibrational energy in liquids and solids.

Accordingly, in Section II we examine the competition between the thermal and photochemical mechanisms of reactions under the influence of infrared radiation and analysed studies at high pressures. Strictly speaking, a considerable proportion of these studies cannot be regarded as photochemical (or "laser-chemical"), but laser heating leads to characteristic features in the kinetics compared with the equilibrium heating by the wall. For this reason, the inclusion of these studies in the present review appears useful. Section III is devoted to the reactions of weakly excited molecules with atoms and free radicals. Section IV deals with the results of studies on the selective dissociation of polyatomic molecules under the influence of the pulsed radiation of infrared lasers. The rates of transformation of vibrational energy into translational and rotational energy and the rates of transfer of vibrational energy between different molecules and different vibrational degrees of freedom of one molecule are very important in all reactions involving vibrationally excited species. Numerous experimental and theoretical studies on this problem are now available in the literature and their analysis requires a special review. For this reason, we confine ourselves to an examination of relaxation processes in molecules whose reactions under the influence of infrared radiation have been investigated in greatest detail (Section V). Section VI is devoted to reactions in the condensed phase and on the surface.

The review does not deal with chemical reactions occurring on evaporation of condensed substances and following electrical breakdown in gases under the influence of infrared radiation. Nor do we consider processes involving multistage dissociation and ionisation, where the infrared laser radiation is used solely in the first stage, and processes associated with a change in properties of vibrationally excited molecules other than their reactivity.

II. COMPETITION BETWEEN THE THERMAL AND PHOTOCHEMICAL MECHANISM OF REACTIONS UNDER THE INFLUENCE OF INFRARED RADIATION

Irradiation of a substance by infrared light is inevitably accompanied by equilibrium thermal heating owing to vibrational-translational ($V-T$) relaxation. The problem therefore arises of the cause of the chemical reaction under the influence of infrared radiation: equilibrium thermal heating or the involvement of more reactive vibrationally excited species generated by the laser radiation.

The competition between the thermal and photochemical mechanisms of the transformation of the given substance under the influence of pulsed laser radiation has been examined in a study[26] where the criteria for the selection of the duration of the laser pulse and its intensity where the reaction proceeds via a non-thermal pathway were formulated. Analysis of the thermal and radiation-induced populations of the excited states when the substance is acted upon by continuous laser radiation[27,28] led to the conclusion that there is a critical pressure above which the radiation-induced population cannot exceed the thermal population whatever the power of the laser emission. This critical pressure depends on the size of the infrared quantum, temperature, thermal conductivity of the mixture, the rate of $V-T$ relaxation, and the ratio of the diameters of the reaction vessel and the laser beam. For processes under the influence of the emission of the CO_2 laser at room temperature and for molecules of moderate complexity, the critical pressure does not exceed 1 mmHg.

The thermal and radiation-induced populations of vibrationally excited states have been analysed[26-28] in terms of a two-level approximation, i.e. without taking into account the vibrational–vibrational ($V-V$) relation processes. In reality these processes lead to a redistribution of vibrational energy among different degrees of freedom of the excited molecules. Since the rate of $V-V$ relaxation usually greatly exceeds the rate of $V-T$ relaxation, the energy undergoes equilibrium distribution among the vibrational degrees of freedom, which may be characterised by the vibrational temperature (different from the translational temperature). The criteria governing the "discrepancy" between the vibrational and translational temperatures and the possibility of carrying out chemical reactions under such conditions have been examined[29-31]. However, this analysis was carried out without taking into account the equilibrium thermal heating due to the infrared radiation. We may note that a complicating factor in the consideration of complex molecules is the high probability of $V-T$ relaxation from high vibrational levels. A general theoretical treatment of the distribution of excited species with respect to different vibrational states is not available in the literature for this case.

The first observations of chemical reactions under the influence of infrared laser emissions were made by French investigators[32-35], who recorded the glow of ammonia, ethylene, ethyl chloride, and their decomposition products under the influence of the emission from a continuous CO_2 laser on the gases at a pressure of several hundred mmHg. The authors themselves attributed the observed chemical reactions to equilibrium thermal heating. Subsequently a number of studies were made on the laser pyrolysis of ethylene[36-39], ammonia[40,41], and other compounds which effectively absorb the radiation generated by the CO_2 laser[42-51]. Analysis of the secondary infrared emission spectra under such conditions shows that they are caused by the heating of the gases in the region of laser irradiation[52-54]. The study of the bimolecular reactions of PF_5 with SO_2[55] and of SF_6 with H_2 and O_2[56] under the influence of the radiation from the CO_2 laser operating under quasi-continuous conditions (with pulses lasting $10^{-2}-10^{-3}$ s) showed that they also proceed via the thermal mechanism.

However, the authors of a number of studies dealing with chemical reactions under the influence of infrared laser radiation under conditions similar to those described above (i.e. at pressures of tens and hundreds of mmHg) hold a different view and attribute the reactions under these conditions to the non-equilibrium population of highly vibrationally excited states of the molecules irradiated by infrared light. These are the reactions of tetrafluorohydrazine with nitrogen oxides, hydrogen, methane, etc.[57-66], the bromination of pentafluorobenzene[67], the reaction of HBr with carboranes[68,69], the decomposition of Freons[70,72], the interaction of diborane with isobutene[73] and hydrogen sulphide[74], the interaction of boron trichloride with tetrachloroethylene[75] and trimethylboron[76], and the pyrolysis of acetylene[77].

One of the principal arguments of the authors of the majority of these studies in support of a non-thermal mechanism of the chemical reactions is higher rates and differences in the composition of the products of chemical reactions under the influence of infrared radiation compared with reactions under the conditions of ordinary heating to the corresponding temperatures. However, the difficulties in the direct measurements of the temperature rise induced by the laser radiation make it necessary to estimate the temperature by calculation, which hinders the comparison of the results corresponding to laser and thermal initiation of the reactions.

Another argument is the observation of threshold phenomena, i.e. a sharp dependence of the reaction rates on the intensity of the laser radiation when the latter is above a threshold value and the virtually complete absence of reactions below the threshold. According to the authors, the presence of the threshold may show that the rate of reaction is determined by the concentration of highly excited species with an energy much higher than the energy of the absorbed quantum. The probability of their formation in $V-V$ relaxation processes depends strongly on the intensity of the infrared radiation, the dependence being described by a power function. If the equilibrium temperature rise due to the infrared radiation is insignificant, the occurrence of threshold phenomena is indeed a serious argument in support of a photochemical process mechanism. However, the occurrence of an equilibrium temperature rise in the irradiated volume may lead to the same behaviour both in consequence of the pronounced exponential temperature dependence of the rates of the majority of chemical reactions and as a result of the initiation of thermal or chain explosion, so that experiments of this kind require careful analysis.

A number of studies have been devoted to detailed analysis of threshold phenomena in reactions under the influence of infrared radiation[60-63]. One should note that in most instances threshold phenomena have been observed in exothermic reactions. The given substance undergoes virtually complete conversion on irradiation with a single pulse despite the fact that only part of the reactor volume is irradiated. Evidently the pulse of infrared radiation initiates the reaction in the irradiated volume, after which it is propagated throughout the reactor. The explosive decomposition of ethyl iodide under the influence of the radiation of a continuous CO_2 laser has been explained[78] within the framework of the theory of thermal explosion initiated by the laser radiation. In the thermally neutral decomposition of monosilane[61] threshold phenomena have been observed less distinctly and the latter can also be accounted for within the framework of a thermal reaction mechanism: the exponential dependence of the rate of reaction on temperature (the temperature increases with increasing radiation intensity) can simulate effectively threshold phenomena. Thus the threshold phenomena cannot themselves serve as an unambiguous demonstration of a photochemical mechanism of reactions under the influence of infrared radiation.

At first sight non-ambiguous evidence for a non-thermal reaction mechanism at high temperatures was obtained in a study[70] where the decomposition of Freon (CF_2Cl_2) was investigated at a pressure of 100 mmHg under the influence of the radiation of a continuous CO_2 laser. We shall consider this study in greater detail. It involves the investigation of the decomposition of Freon mixed with SF_6. The infrared absorption bands of CF_2Cl_2 and SF_6 are separated by 17 cm^{-1}. When the laser is tuned to a frequency of 948 cm^{-1}, corresponding to the absorption maximum of SF_6, Freon does not absorb the infrared radiation and, conversely, when the laser is tuned to $\nu_{max} = 931$ cm^{-1} for CF_2Cl_2, SF_6 does not absorb. The SF_6 and CF_2Cl_2 pressures (4.4 and 100 mmHg respectively) were chosen so that the absorption of the infrared radiation by the mixture was the same in the above two experiments, which should have led to identical temperature distributions. If the reaction mechanism is thermal, the nature of the transformations should be independent of whether SF_6 or CF_2Cl_2 absorbs. It was shown experimentally that, when the laser is tuned to the SF_6 absorption, frequency the reaction does not occur (SF_6 is itself stable up to very high temperatures), whereas, on tuning the laser to the absorption frequency of CF_2Cl_2, the latter decomposes. The authors[70] conclude that the decomposition of Freon is due to its vibrational excitation and not to the temperature rise.

Although this conclusion is outwardly self-evident, detailed analysis has shown[43] that it is not unambiguous. In these experiments the absorption coefficients on which the calculation of the SF_6 and CF_2Cl_2 pressures necessary to equalise the absorptions was based were determined at room temperature with the aid of a low-power CO_2 laser. On passing to more powerful infrared radiation, where the gas is appreciably heated, the infrared absorption spectra change owing to the appearance of "hot" bands. Furthermore, it is easy to show[43] that the SF_6 absorption maximum undergoes a bathochromic shift under these conditions. This leads to a greater temperature rise in the mixture when the laser is tuned to 931 cm^{-1}, which is sufficient for the decomposition of Freon by a thermal mechanism. The results of the above study[70] as well as those of other investigations of chemical reactions under the influence of infrared radiation at high pressures have been analysed in detail[43] and it has been concluded that the evidence for a non-thermal mechanism of the laser-chemical reactions under these conditions is not sufficiently established.

As regards the differences in the composition of the products of laser-chemical reactions at high pressures, it has been shown[43] that they can be due to the exclusion of heterogeneous processes, because the reactor walls remain cold on laser heating. A number of studies involving the pyrolysis of ethane[44,45], formic acid[46], formaldehyde[47], methanol[48], and other compounds as well as the interaction of boron trichloride with acetylene[49], the bromination of pentafluorobenzene[50,67], and other reactions[51] have been devoted to the problem of the characteristic features of chemical reactions on laser heating[43-51]. Since not all substances absorb infrared radiation, they are frequently sensitised by compounds which absorb effectively the radiation of the CO_2 laser, mainly SF_6. In the majority of investigations it is emphasised that laser heating makes it possible to carry out reactions under rigorously homogeneous conditions. This permits the determination of the rate constants and activation energies for the reactions, which under the conditions of ordinary heating are complicated by heterogeneous side reactions[43,46-48,50].

The exclusion of heterogeneous processes in the laser heating of gases at high pressures is apparently one of the main factors responsible for the unusual products of the chemical reactions. (The formation of mercaptoboranes[74], the reactions of tetrafluorohydrazine[57,58,64], the alkylation of diborane[73], etc.) Thus analysis of the experimental data for gas-phase reactions at pressures of tens and hundreds of mmHg under the influence of continuous and quasi-continuous (with pulses lasting 10^{-3}–10^{-2} s) laser irradiation shows that under these conditions chemical reactions take place mainly via a thermal mechanism. Laser heating can then lead to an alteration of the mechanisms of complex chemical reactions owing to the exclusion of heterogeneous processes. This can be used both for preparative purposes and for the investigation of quantitative kinetic relations governing the homogeneous stages of complex chemical reactions.

In order to avoid the influence of thermal heating on the rate of chemical reactions in systems acted upon by the radiation of continuous infrared lasers, it is necessary to carry out the processes at low pressures[27,28]. This has been confirmed experimentally by a study[79] in which the influence of the radiation of a continuous CO_2 laser on the induction period in the chain decomposition of chlorine dioxide was studied. At pressures more than 1 mmHg the induction period was shortened, i.e. the reaction was accelerated, due to the equilibrium thermal heating as a result of the absorption of the infrared radiation. However, at pressures below 1 mmHg, the induction period for the decomposition of ClO_2 increased under the influence of the laser radiation, which was explained by the acceleration of the $ClO + ClO_2 \rightarrow Cl_2O_3$ elementary stage owing to the vibrational excitation of the ClO_2 molecule; this leads to an increase of the induction period.

Low pressures limit the range of reactions susceptible to such investigations. It is necessary that the reaction should occur at a sufficient rate at low pressures (below 1 mmHg). The activation energy for such a reaction must be fairly low. Among molecular reactions satisfying this requirement, mention may be made of the decomposition of limonene at low pressures[42] and the decomposition of H_3BPF_3 under the influence of the radiation of a continuous CO_2 laser[80,81]. When the latter reaction was carried out at pressures in the range 10^{-3}–10^{-2} mmHg, the authors were able to observe isotopic selectivity with respect to both hydrogen and boron.

III. REACTIONS OF VIBRATIONALLY EXCITED MOLECULES WITH ATOMS AND FREE RADICALS

Reactions with low activation energies are convenient for the investigation of infrared photochemistry for two reasons. Firstly, their high rates make it possible to carry them out at low pressures, which permits investigations under conditions uncomplicated by equilibrium thermal heating. Secondly, for low activation energies, comparable with the energies of the infrared quantum, it is possible to ensure conditions where only vibrationally excited molecules, formed in the primary radiation absorption step, are involved in the reaction and the role of higher vibrationally excited states, arising in $V-V$ relaxation processes, is insignificant. One can then expect a high process selectivity owing to the differences between the infrared absorption spectra of the excited molecules.

The most common processes with low activation energies are those of atoms and free radicals with molecules. One of the problems in the study of the influence of infrared radiation on these reactions is that of the role of vibrational energy in overcoming the activation barrier. Here it is necessary to distinguish two situations. At very low concentrations of the absorbing gas, where the $V-V$

relaxation is slower than that $V-T$ relaxation and the reaction, it is possible to obtain information about the reactivities of individual excited states. At higher concentrations (which are nevertheless sufficiently low to rule out equilibrium thermal heating), where equilibrium is established between all the vibrational degrees of freedom and one can postulate vibrational heating, one may investigate the influence of vibrational temperature on the reaction at a fixed translational temperature.

A promising practical application of these studies involves chemical reactions which are selective with respect to isotopes. The isotopic selectivity may be not only the aim of the investigation but can also serve as a test of the reactivity of the excited isotopic molecule. In view of the high rates of exchange of vibrational energy between the isotopic molecules, the concentrations over which such processes are possible will be fairly low.

One of the first studies which demonstrated experimentally the increase of reactivity under the conditions of laser infrared excitation was that of Brooks and coworkers[82]. They recorded an increase by two orders of magnitude of the cross-section of the K + HCl → KCl + H reaction in a molecular beam on excitation of HCl by the radiation of a chemical HCl laser. The study of the role of translational energy in this reaction showed[83] that the reaction cross-section increases only by a factor of five for a corresponding increase in translational energy.

The rate of reaction of a vibrationally excited HCl molecule ($v = 1$), generated by a chemical HCl laser, with hydrogen and oxygen atoms has been measured[84,85]. The infrared fluorescence of HCl ($v = 1$) was recorded and at the same time measurements were made of the concentrations of H and O atoms. The study of the simultaneous decrease of fluorescence intensity yields the sum of the rate constants for relaxation by atoms, namely $O + HCl (v = 1) \rightarrow O + HCl (v = 0)$, and for the reaction $O + HCl (v = 1) \rightarrow OH + Cl$, while the measurement of the decrease in the concentration of atoms makes it possible to determine the reaction rate constant. The overall rates of disappearance of vibrationally excited HCl molecules ($v = 1$) have been measured[84] and it has been shown that, following interaction with hydrogen atoms, the rate of the reaction $H + HCl (v = 1) \rightarrow H_2 + Cl$ is negligibly small compared with the rate of relaxation, whereas following interaction with oxygen atoms its contribution is appreciable. Detailed measurements have shown[85] that the rate of reaction of HCl ($v = 1$) with oxygen atoms is lower by a factor of 20 than the rate of relaxation and that the reaction rate constant is $(1.1 \pm 0.3) \times 10^{11}$ cm^3 mole^{-1} s^{-1}. This made it possible to calculate the ratio of the rate constants for the reaction of oxygen atoms with an HCl molecule in the first vibrationally excited and ground states, which amounts to 300 ± 100. It is noteworthy that in this instance the HCl excitation energy (8.2 kcal mole^{-1}) greatly exceeds the activation energy for the reaction with oxygen atoms (4.5 kcal mole^{-1}), so that the maximum expected increase of the rate constant for a vibrationally excited molecule (at 300 K) is by a factor $\exp(4500/RT) = 1.8 \times 10^4$. The measured increase of the rate constant (by a factor of 300) shows that in this reaction the vibrational energy is not fully utilised to overcome the activation barrier.

The measurement of the rate constants for the reactions of vibrationally excited species is greatly simplified if one of the reaction products is also an excited species. In this case it is possible to use the highly sensitive and rapid technique involving the recording of its luminescence. The reactions of vibrationally excited ozone molecules with NO and SO have been studied[86-93]. They lead to the formation of electronically excited NO_2 (in the $^2B_1$ and $^2B_2$ states) and SO_2 ($^1B_1$) molecules, the luminescence of which was recorded. The vibrational excitation of ozone was achieved by means of the radiation of a continuous CO_2 laser which was modulated by a chopper. The luminescence signal of the electronically excited reaction products was also found to be modulated. At the same time the decrease in signal intensity is determined by the sum of the rate constants for relaxation and the reaction and the degree of modulation is determined by the rate constant for the reaction of the vibrationally excited molecules. The rate constants for the reactions of the vibrationally excited ozone molecules with NO and SO measured under these conditions exceed the corresponding values for the non-excited ozone molecules by factors of 5.6 and 2.5. Such low factors can probably be accounted for by the markedly exothermic nature of these reactions. It is not clear whether the acceleration of the reactions should be attributed to the reactivity of the excited state of the ozone molecule (ν_3 antisymmetric stretching vibration) or to the redistribution of the absorbed energy over all the vibrational states of O_3 under the conditions of these experiments.

The reaction of O_3 with NO is of interest because the NO molecule can also be vibrationally excited ($v = 1$) by the radiation of the CO laser (1884 cm^{-1}). Such experiments[94] led to an increase of the reaction rate constant by a factor of 5.7 after the vibrational excitation of NO. In this case one may confidently speak of the reactivity of the NO molecule in the first vibrationally excited state.

An analogous method (with excitation by a CO_2 laser) has been used to investigate the reactions of vibrationally excited O_3 with oxygen in the $^1\Delta_g$ state[90] and also to investigate the reactions of atomic oxygen with vibrationally excited C_2H_4 and OCS molecules[95]. In the latter case both direct excitation of the molecules by the radiation of the CO_2 laser and excitation via sensitisers (molecules with high absorption coefficients for the laser radiation, in the present instance CH_3F and CH_2F_2) was achieved.

The use of the rapid luminescence technique for the recording of reaction rates is difficult in reactions leading to the formation of non-excited products. The study of the decrease of the infrared luminescence signal due to a vibrationally excited molecule yields the sum of the rates of reaction and relaxation. The determination of the reaction rate from these data involves considerable experimental difficulties and becomes impossible if the rate of relaxation is much higher than the rate of reaction (see, for example, Refs. 84 and 85). In endothermic reactions, where one may expect a considerable influence of the vibrational excitation, the products are usually non-excited. The most direct way of investigating such reactions involves the direct measurement of the relative increase in reaction rates under the influence of the radiation of continuous lasers. Mass spectrometry is a convenient method for the measurement of reaction rates. Low pressures in the reactor make it possible to connect it via a leak valve to the ion source and to record the change in the concentration of the initial substances and reaction products directly in the course of the process.

This method has been used to investigate the influence of the vibrational excitation of methane on its reaction with atomic chlorine[96]. The methane molecule was excited by the radiation of a continuous He–Ne laser at a wavelength of 3.39 μm, the corresponding frequency being the same as that of the antisymmetric stretching vibration of CH_4. The comparatively low power of the laser (up to 80 MW) nevertheless made it possible to obtain a concentration of the vibrationally excited molecules higher than the equilibrium value by a factor of several units at room temperature and by several orders of magnitude at 150 K. However, no increase was recorded in the reaction rate under the influence of infrared radiation, within the limits of experimental accuracy. Hence it was concluded that the vibrational energy is relatively ineffective in overcoming the activation barrier in this virtually thermally neutral reaction. The low isotope effect (~ 3% with respect to bromine) in the analogous CH_3Br chlorination reaction under the influence of the radiation of the CO_2 laser is probably associated with the same factor[97].

The above method has also been applied to the study of the endothermic reaction of bromine atoms with CH_3F.[98,99] The vibrational excitation was achieved by the radiation of a continuous CO_2 laser having a power up to 20 W. An increase in the reaction rate by a factor of several units at CH_3F pressures amounting to tenths and hundredths of mmHg was recorded in these experiments. Special experiments showed that under these conditions the increase in reaction rate is not associated with equilibrium thermal heating but is caused by the superequilibrium concentration of the vibrationally excited molecules generated by the laser radiation. The study of the dependence of the rate of reaction on the power of the laser emission has shown that at low CH_3F pressures it is linear, but, as the pressure rises, the rate increases more rapidly with increase in the power. Hence one may conclude that, under linear conditions, the lowest vibrationally excited states of the CH_3F molecule (with an energy of ~3 kcal mole^{-1}) are responsible for the increase of the reaction rate. An increase in pressure increases the role of higher vibrationally excited states formed when the species initially generated by the laser emission collide with one another; this leads to a more pronounced dependence of the reaction rate on the power. As the pressure in an equimolar mixture of $^{12}CH_3F$ and $^{13}CH_3F$ was reduced to values for which there is insufficient time to establish vibrational equilibrium between the excited and non-excited isotopic molecules (~10^{-2} mmHg), a doubling of the rate of formation of the reaction product containing the carbon isotope present in the CH_3F molecule excited by the laser emission was recorded[99].

The bromination of CH_3F is of interest also because, depending on the wavelength of the light causing the dissociation of the Br_2 molecule into atoms, the latter are formed in both ground (${}^2P_{3/2}$) and excited (${}^2P_{1/2}$) states with an excitation energy of ~10.5 kcal mole^{-1}. At low pressures the atoms in both states make comparable contributions to the reaction. It has been shown[100] that electronic excitation of the bromine atom reduces the activation energy for its reaction with CH_3F by the excitation energy, with a simultaneous decrease of the pre-exponential factor by 2.6 orders of magnitude. Photobromination of CH_3F under the influence of ultraviolet light at different wavelengths and study of the influence of infrared radiation on the reaction showed that the vibrational energy is effectively utilised in the endothermic reaction of the bromine atom in its ground state and has no influence whatever on the virtually thermally neutral reaction of the electronically excited bromine atom[101].

It is noteworthy that the low efficiency of the utilisation of the vibrational energy in overcoming the activation barrier in exothermic and thermally neutral reactions is consistent with data on the formation of vibrationally excited species in exothermic reactions. Such processes underlie the operation of chemical lasers and are the converse of those discussed in the present section.

Reactions involving the formation of vibrationally excited species with energies greater than the heats of reaction are at present virtually unknown[102]. It follows from the principle of detailed balancing that in the reverse processes the vibrational energy plays a significant role in overcoming only the endothermic part of the activation barrier, while the remaining energy must be translational or rotational. Theoretical calculations of the rate constants for model interactions of atoms with diatomic molecules[103] also showed that vibrational energy should play a significant role in endothermic reactions and a much smaller role in thermally neutral reactions and, particularly, exothermic reactions, where the barrier must be overcome mainly by translational energy. Analysis of the available experimental data for the reactivity of vibrationally excited molecules[104,105] shows that in the vast majority of instances vibrational energy is not fully utilised in overcoming the activation barrier. The attempts to relate the fraction of the vibrational energy effectively employed in overcoming the activation barrier of the reaction to the size of the barrier, the heat of reaction, or the size of the vibrational quantum[104] have not as yet established any empirical relations. It appears that the number of reliable experimental rate constants for the elementary reactions of vibrationally excited molecules is still insufficient. The most reliable of the available experimental data, obtained by infrared laser photochemical methods, are presented in Table 1.

Table 1. Reactions of vibrationally excited molecules with atoms and free radicals.

Reaction	ΔH, kcal mole^{-1}	E, kcal mole^{-1}	hν, kcal mole^{-1}	$\left(\frac{k^*}{k}\right)_{calc}$	$\left(\frac{k^*}{k}\right)_{expt}$	Refs.
$HCl^*(v=1)+O \rightarrow OH + Cl$	0.8	4.5	8.2	$1.8\cdot10^4$	300	85
$C_2H_4^* + O \rightarrow CH_3 + CHO$	—30.9	—	3.0	$1.5\cdot10^2$	1.5	95
$OCS^* + O \rightarrow CO + SO$	—53.5	5.8	3.0	$1.5\cdot10^2$	3.0	95
$O_3^*(\nu_{1,2,3}) + SO \rightarrow SO_2(^1B_1) + O_2$	—25	—	3.0	$1.5\cdot10^2$	2.5	88
$O_3^*(\nu_{1,2,3}) + O_2(^1\Delta_g) \rightarrow 2O_2 + O$	1.4	—	3.0	$1.5\cdot10^2$	38	90
$O_3^*(\nu_{1,2,3}) + NO \rightarrow NO_2(^2B_1) + O_2$	—20.0	4.2	3.0	$1.5\cdot10^2$	5,6	90
$O_3^*(\nu_{1,2,3}) + NO \rightarrow NO_2(^2A_1) + O_2$	—48.0	2.3	3.0	40	17,1	90
$NO^*(v=1) + O_3 \rightarrow NO_2(^2B_1) + O_2$	—20.0	4.2	5.4	$1.1\cdot10^3$	5.7	94
$CH_4^*(\nu_4) + Cl \rightarrow HCl + CH_3$	—1.0	3.8	3.7	$3\cdot10^5$ (150 K)	<30	96
$CH_4^*(\nu_3) + Cl \rightarrow HCl + CH_3$	—1.0	3.8	8.6	$2\cdot10^5$ (150 K)	$<10^3$	96
$CH_3F^*(\nu_{3,6}) + Br(^2P_{3/2}) \rightarrow HBr + CH_2F$	12.0	14.6	3.0	56 (373 K)	30	98
$CH_3F^*(\nu_{3,6}) + Br(^2P_{1/2}) \rightarrow HBr + CH_2F$	1.5	4.5	3.0	56 (373 K)	1	101

Note. $(k^*/k)_{calc} = \exp(h\nu/RT)$ for $h\nu < E$ and $\exp(E/RT)$ for $h\nu > E$, ΔH is the heat of reaction, and E and $h\nu$ are respectively the activation and excitation energies.

A number of studies on the effect of infrared laser emission on the reactions of atoms with molecules were undertaken specially to achieve chemical reactions selective with respect to isotopes. One of the first attempts to achieve such a process was undertaken by Mayer et al.[106] A mixture of CH_3OH, CD_3OD, and Br_2 at 70 mmHg was exposed to the emission of a continuous HF laser with a power of 90 W, which is selectively absorbed by the CH_3OH molecule, while CD_3OD does not absorb such emission. After irradiation for 1 min, 90% of CH_3OH was converted into CH_2O, while CD_3OD hardly reacted under these conditions. The rate-limiting step of the process is the reaction of the bromine atom with CH_3OH, the activation energy for which is 6.2 kcal mole^{-1}. Since the energy of the quantum of the HF laser (10.4 kcal mole^{-1}) exceeds the above value, the authors concluded that they observed the reaction of a vibrationally excited CH_3OH molecule with a bromine atom, which thus proceeds without activation energy, in contrast to the non-excited CD_3OD molecule. This leads to a high isotopic selectivity of the given reaction. However, the above conclusion is doubtful, because at the high pressures employed (i.e. for high rates of $V-T$ relaxation) it is difficult to expect appreciable deviations of the populations of the vibrationally excited molecules from the equilibrium values and the results may be accounted for by a kinetic isotope effect. Special experiments on the chlorination of a mixture of CH_4 and CD_4 by the emission of a continuous CO_2 laser, carried out at the same pressures as in the study of Mayer et al.[106], showed[107] that mainly CH_4 molecules are involved in the reaction, although the laser emission is absorbed by the CD_4 molecule. Detailed measurements of the quantum yield of the reaction in a methanol–bromine mixture under the influence of infrared radiation[108] also failed to confirm the conclusions of Mayer et al.[106]

More evident successes in carrying out an isotopically selective reaction were achieved by Arnoldi et al.[109] and Leone et al.[110] By exciting an $H^{35}Cl$ molecule to the second vibrational level using the emission of a pulsed chemical HCl laser[109] and a parametric oscillator[110], it was possible to carry out a $Br + H^{35}Cl \rightarrow HBr + {}^{35}Cl$ reaction selective with respect to chlorine isotopes. However, rapid secondary radical processes precluded an isotopic enrichment of the final reaction product.

The chlorination of CH_3Br [97] (selectivity with respect to bromine isotopes) and the bromination of CH_3F [99] (selectivity with respect to carbon isotopes) are examples of processes in which isotope enrichment was achieved in the final products under the influence of the emission of a continuous CO_2 laser.

IV. SELECTIVE DISSOCIATION OF POLYATOMIC MOLECULES UNDER THE INFLUENCE OF PULSED INFRARED RADIATION

The selective dissociation of molecules (as well as other reactions with high activation energies), requiring the absorption of many infrared photons, initially appeared to be virtually impossible to achieve. Indeed when the infrared laser emission is absorbed, the products are molecules with a low degree of excitation which are incapable of absorbing radiation at the same frequency owing to vibrational anharmonicity. Higher vibrationally excited states may arise on collision of the initially excited molecules with one another, i.e. in a $V-V$ relaxation process. At high emission intensities this can lead to specific reactions, but the selectivity attainable in the primary absorption step must be lost in the course of the $V-V$ processes.

Letokhov and Ambartsumyan observed that the above difficulties may be overcome by employing a powerful pulsed infrared emission. This discovery greatly extended the likely applications of infrared lasers both in carrying out isotopically selective chemical reactions and in the development of vibrational photochemistry.

The first evidence for the possibility of multiphoton absorption was obtained in studies[111,112] where luminescence was observed in the visible and infrared regions of the spectrum, due to the rapid dissociation of NH_3, SiF_4, and CCl_2F_2 molecules under the influence of the focussed emission of a powerful pulsing CO_2 laser. Later analogous results were obtained also in studies of the dissociation of other compounds[113-116]. The study of the luminescence kinetics showed[117-119] that two stages are observed: a rapid stage arising immediately after the pulse of the infrared radiation and a slow stage due to collisions. It has been shown[120-122] that, when many compounds are irradiated by powerful pulses from a CO_2 laser, not only dissociation but also ionisation takes place.

Ambartsumyan et al.[118] showed for the first time that dissociation in the field of the emission from a powerful pulsed CO_2 laser is isotopically selective. The luminescence due to the ^{10}BO and ^{11}BO radicals, formed as a result of the irradiation of BCl_3 having the natural isotope composition in an oxygen atmosphere, was recorded, the enrichment coefficient in the BO intermediate reaching 10 under these conditions. Soon the above method led to isotope enrichment of the final products of the dissociation of SF_6,[123,124] BCl_3,[125] OsO_4,[126] and CCl_4.[127] Subsequently such experiments on the isotopically selective dissociation of polyatomic molecules were reproduced in many laboratories for the same and a number of new systems [128-134] and many experimental and theoretical studies, devoted to the detailed investigation of the mechanism of this phenomenon, were published[135-169].

The fundamental feature of these investigations was the elucidation of the problem of compensating the vibrational anharmonicity, which must lead to the breakdown of the conditions for the resonance absorption of infrared radiation after the absorption of the first quantum. The initial explanations reduced to the Stark broadening of the frequencies of vibrational transitions in the strong field of the infrared radiation[118-124]. However, calculations showed[169] that this requires a much higher radiation intensity than those for which selective dissociation is observed. Next the hypothesis was put forward that compensation of the anharmonicity is required only for a few of the lowest vibrational transitions (3–4 for molecules such as those of SF_6, BCl_3, etc.), where the vibrational spectrum has a discrete structure, while in higher vibrational transitions the density of the levels increases so much that they form a quasi-continuum[138,141]. Experiments on two-frequency dissociation[138-141], in which molecules were excited by resonance infrared radiation to a few of the initial levels and dissociation was achieved by means of non-resonance infrared radiation absorbed in the quasi-continuum, confirmed this view. According to the proposed hypothesis[138,141], the vibrational anharmonicity in the lowest transitions is compensated as a result of rotational energy; the first, second, and third quanta of infrared radiation are resonance-absorbed by one of the rotational lines of the P-, Q-, and R-branches of the vibrational transition respectively. The dependence of the probability of dissociation on the frequency of the resonance infrared radiation is consistent with this hypothesis.

However, only some of the molecules in specific rotational states are involved in vibrational energy accumulation processes when this mechanism operates. On the other hand, measurements of the number of molecules dissociating under the influence of infrared radiation have shown that in the region of the focus of the light beam virtually all the molecules are dissociated by a single pulse. For this reason, in the latest studies on this problem the anharmonic splitting of overtones[147], the removal of the degeneracy of the vibrational levels in symmetrical molecules[154,164], and forced transitions between various rotational levels[153] were additionally invoked to account for the compensation of the vibrational anharmonicity in the lowest transitions.

One of the causes of the loss of selectivity (for fairly large isotopic shifts) is $V-V$ relaxation processes, so that a high selectivity in multiphoton dissociation is achieved only at low pressures (below 1 mmHg). Another cause may be secondary radical reactions, lowering the selectivity of the primary dissociation step. For example, it has been shown that the formation of active species such as fluorine atoms in the primary dissociation step may lead to a decrease of selectivity[170,171]. For this reason, the study of the chemical mechanism of the primary dissociation step is of great interest.

The discovery of multiphoton absorption of intense infrared radiation "without collisions" leads to new interesting possibilities in the study of the unimolecular decomposition of molecules with a large excess of energy. Among these, mention should be made in the first place of the possibility of observing non-statistical unimolecular decomposition of vibrationally excited species and decomposition in states whose energy greatly exceeds the dissociation threshold. Bimolecular reactions involving such highly excited molecules may also be of great interest. At the present time the number of studies published on the mechanisms of reactions of highly vibrationally excited molecules is much smaller than the number of studies on isotopically selective dissociation. Among these, mention should be made of the decomposition of alkyl halides [172], the reactions of methyl halides with halogens[173,174], and the *cis-trans* isomerisation of $C_2H_2Cl_2$ [175] and deuterohexadienes[176]. The dissociation due to vibrational excitation proceeds by no means in all cases via fundamentally new chemical reaction pathways. Thus it has been shown[177] that, when pulsed infrared radiation acts on mixtures of SF_6 with hydrocarbons, the latter react with the fluorine atoms formed on dissociation of SF_6. The chemical reactions of molecules which do not absorb the infrared laser emission are of great interest. In this case the reaction may be achieved as a result of the transfer of vibrational energy from molecules which effectively absorb the infrared emission. An examples of such a process may be the decomposition of 1,2-dihydroxytetramethylethane into two acetone molecules as a result of the transfer of vibrational energy from a CH_3F molecule, excited by the emission of a pulsed CO_2 laser, to a molecule of 1,2-dihydroxytetramethylethane[178].

The processes examined may also be of preparative interest. The synthesis of $BHCl_2$ from BCl_3 and H_2 was achieved[179] on irradiating a mixture of the latter two substances by the pulses of a CO_2 laser. It has been stated[180] that it is likely to be useful to dissociate small amounts of impurities in order to achieve a high degree of purification of the main substance; arsenic trichloride was freed in this way from 1,2-dichloroethane and carbon tetrachloride.

The vast majority of processes considered in this section have been achieved with the aid of the emission from a CO_2 laser. This is the most powerful, economical, and simplest gas laser to operate. It can operate on different lines in the range 9.4–10.6 μm (the use of isotopic modifications of CO_2 such as $^{13}CO_2$ or $^{12}C^{18}O^{16}O$ extends this range to 8.5–10.6 μm). However, not all the molecules which are of theoretical or practical interest have absorption lines in this region. Diatomic homonuclear molecules such as H_2, N_2, O_2, and others cannot be vibrationally excited by infrared radiation at all. The phenomenon of stimulated Raman scattering (SRS) may be used to excite such molecules. When a pulse of laser emission in the ultraviolet, visible, or near infrared range is passed through a cuvette with a gas at a high pressure, then a Stokes component, the energy of the quantum of which is lower than the energy of the initial quantum by the energy of the vibrational quantum of the substance in the cuvette, appears at the exit together with the transmitted emission. The interaction of these two types of emission, having different frequencies, with the same substance in the following cuvette leads to its vibrational excitation.

The idea of using SRS for isotope separation has been suggested[181]. This process was achieved experimentally in the formation of NO by the reaction of N_2 or O_2.[182] The vibrational excitation of N_2 was achieved with the aid of SRS in liquid nitrogen. The absorption coefficient with respect to nitrogen-15 reached 10^2 under these conditions. The same result was also obtained in the excitation of a mixture of N_2 and O_2 in a pulsed electric discharge[183]. The authors[182] explained it by the establishment of different vibrational temperatures of $^{14}N_2$ and $^{15}N_2$ under the conditions of the experiment described. However, in analogous experiments in a discharge tube an enrichment of 21% with respect to nitrogen-15 was attained[184]. In order to resolve this discrepancy, additional studies are necessary.

At the same time, using SRS it is possible to achieve the vibrational excitation of molecules which do not absorb infared radiation. This technique permits an alteration of the laser frequency and its displacement to the regions where sufficiently powerful infrared lasers are not available. Hydrogen-based SRS has been used to dissociate SF_6 in the region of the $\nu_4 + \nu_5$ combination band[185], which made it possible to increase the process selectivity.

V. RELAXATION AND VIBRATIONAL ENERGY TRANSFER PROCESSES

The main processes competing with the reactions of vibrationally excited molecules are the $V-T$ and $V-R$ relaxation processes leading to the loss of vibrational energy and the $V-V$ relaxation processes leading to its redistribution between different molecules and between vibrational degrees of freedom within the same molecule. In most cases the vibrationally excited species react more slowly than they relax, so that the rate of the relaxation processes must be compared with the rate of generation of vibrationally excited species (proportional to the intensity of the infrared radiation and the absorption coefficient) in order to determine the conditions under which a non-equilibrium population of the corresponding excited state is possible. Before lasers became available, the main sources of information about the relaxation of vibrational excitation were experiments in shock tubes and by acoustic methods as well as kinetic spectroscopy. When infrared laser became available, the above possibilities were greatly extended. The problems of the relaxation of vibrational excitation have been described in a number of review articles and monographs[186-190].

The method of infrared luminescence induced by the laser emission, first used to measure the vibrational relaxation of CO_2,[191] and the double resonance method employed for the measurement of the rates of transfer of vibrational energy in SF_6,[192] BCl_3,[193] and CH_3F [194-196] are most widely employed to investigate the relaxation and vibrational energy transfer processes. The first method involves the observation of the time dependence of the luminescence originating from different vibrational levels and arising after the excitation of the molecule by an infrared pulse. In order to record the spectral dependence of the luminescence, different infrared detectors, cooled to low temperatures, are used. The luminescence originating from different vibrational states is isolated by means of combinations of interference filters. In addition, the filters protect the infrared detector from scattered laser emission, the intensity of which greatly exceeds the luminescence intensity. The recorded signal is usually weak, but the high frequency of the pulses from modern infrared lasers (mainly the CO_2 laser and optical parametric oscillators) makes it possible to use signal accumulation techniques in order to improve the signal to noise ratio.

The double resonance method involves the observation of the changes in the infrared absorption at a fixed frequency when the molecule is excited by an infrared pulse at another frequency. The possibility of using long absorption cells (in contrast to the infrared luminescence method) and hence of reducing the pressure of the gas investigated makes this procedure preferable in the study of rapid processes such as the resonance transfer of vibrational energy between isotopic molecules.

The rates of relaxation processes in a large number of molecules have been investigated in detail with the aid of the above methods. The rate constant for the $V-T$ and $V-V$ relaxation processes for SF_6, BCl_3, HCl, O_3, and CH_3F molecules, the laser-induced chemical reactions of which have been studied in greatest detail, are presented in Table 2. Analysis of the available experimental data shows that the $V-T$ relaxation involving the molecules takes place comparatively slowly and usually requires 10^2-10^5 collisions. The rate-limiting stage of the $V-T$ relaxation is the deactivation of the lowest vibrationally

Table 2. The relaxation and vibrational energy transfer processes for molecules whose reactions under the influence of infrared radiation have been investigated in greatest detail (k is the rate constant and n the number of collisions).

Process	k, $cm^3\ mole^{-1}\ s^{-1}$	n	Refs.
$SF_6(\nu_6) + SF_6(O) \rightarrow 2SF_6(O) + 363\ cm^{-1}$	$1.5\cdot10^{11}$	$2.2\cdot10^3$	192
	$1.2\cdot10^{11}$	$2.9\cdot10^3$	197
$SF_6(\nu_6) + Ar \rightarrow SF_6(O) + Ar + 363\ cm^{-1}$	$4.0\cdot10^{10}$	$3.4\cdot10^3$	192
$SF_6(\nu_6) + He \rightarrow SF_6(O) + He + 363\ cm^{-1}$	$4.6\cdot10^{11}$	$9\ 1\cdot10^2$	192
$SF_6(\nu_i) + SF_6(\nu_k) \rightleftarrows SF_6(\nu_l) + SF_6(\nu_m) + \Delta E$	$1.3\cdot10^{13}$	12	197
	$1.7\cdot10^{13}$	9	198
$BCl_3(\nu_4) + BCl_3(O) \rightarrow 2BCl_3(O) + 243\ cm^{-1}$	$3.2\cdot10^{12}$	$1.5\cdot10^2$	193
$BCl_3(\nu_4) + Ar \rightarrow BCl_3(O) + Ar + 243\ cm^{-1}$	$8.5\cdot10^{10}$	$2.2\cdot10^3$	193
$BCl_3(\nu_4) + He \rightarrow BCl_3(O) + He + 243\ cm^{-1}$	$2.9\cdot10^{11}$	$1.9\cdot10^3$	193
$BCl_3(\nu_i) + BCl_3(\nu_k) \rightleftarrows BCl_3(\nu_l) + BCl_3(\nu_m) + \Delta E$	$3.7\cdot10^{13}$	13	193
$HCl(v=1) + HCl(v=0) \rightarrow 2HCl(v=0) + 2886\ cm^{-1}$	$1.6\cdot10^{10}$	$7.9\cdot10^3$	199
$HCl(v=1) + He, Ne, Ar \rightarrow HCl(v=0) + He, Ne, Ar + 2886\ cm^{-1}$	$<3.7\cdot10^7$	$>3.3\cdot10^6$	199
$HCl(v=2) + HCl(v=0) \rightleftarrows 2HCl(v=1) - 102\ cm^{-1}$	$1.9\cdot10^{12}$	65	200
$H^{35}Cl(v=1) + H^{37}Cl(v=0) \rightleftarrows H^{35}Cl(v=0) + H^{37}Cl(v=1) + 2\ cm^{-1}$	$2.0\cdot10^{13}$	10	200
$HCl(v=1) + Cl \rightarrow HCl(v=0) + Cl + 2886\ cm^{-1}$	$4.2\cdot10^{12}$	18	201
	$5.3\cdot10^{12}$	15	202
$HCl(v=1) + Br \rightarrow HCl(v=0) + Br + 2886\ cm^{-1}$	$1.6\cdot10^{11}$	$4.6\cdot10^2$	201
$HCl(v=1) + O \rightarrow HCl(v=0) + O + 2886\ cm^{-1}$	$2.2\cdot10^{12}$	33	203
$HCl(v=1) + H \rightarrow HCl(v=0) + H + 2886\ cm^{-1}$	$4.6\cdot10^{12}$	46	204
	$3.9\cdot10^{12}$	57	94
$HCl(v=1) + D \rightarrow HCl(v=0) + D + 2886\ cm^{-1}$	$6.5\cdot10^{12}$	25	204
$O_3(\nu_3) + O_3(O) \rightarrow 2O_3(O) + 1042\ cm^{-1}$	$3.8\cdot10^{10}$	$4.6\cdot10^3$	205
$O_3(\nu_3) + Ar \rightarrow O_3(O) + Ar + 1042\ cm^{-1}$	$5.0\cdot10^9$	$3.0\cdot10^4$	93
	$4.0\cdot10^9$	$3.7\cdot10^4$	89, 205
$O_3(\nu_3) + He \rightarrow O_3(O) + He + 1042\ cm^{-1}$	$3.6\cdot10^{10}$	$8.0\cdot10^3$	89, 93
	$4.0\cdot10^{10}$	$7.2\cdot10^3$	205
$O_3(\nu_3) + O_2 \rightarrow O_2(O) + O_2 + 1042\ cm^{-1}$	$1.5\cdot10^{10}$	$1.1\cdot10^4$	93
	$8.0\cdot10^9$	$2.0\cdot10^4$	89
	$1.2\cdot10^{10}$	$1.4\cdot10^4$	205
	$1.1\cdot10^{10}$	$1.4\cdot10^4$	92
$O_3(\nu_3) + NO_2 \rightarrow O_3(O) + NO_2 + 1042\ cm^{-1}$	$7.5\cdot10^{10}$	$2.4\cdot10^3$	93
$O_3(\nu_1, \nu_3) + O(^3P) - \left\lvert \begin{array}{l} \rightarrow O_3(\nu_2) + O(^3P) + 370\ cm^{-1} \\ \rightarrow 2O_2 \end{array} \right.$	$(6\div9)\cdot10^{12}$	$10\div15$	206
$O_3(\nu_2) + O(^3P) - \left\lvert \begin{array}{l} \rightarrow O_3(O) + O(^3P) + 700\ cm^{-1} \\ \rightarrow 2O_2 \end{array} \right.$	$(1\div2)\cdot10^{12}$	$50\div100$	206
$CH_3F(\nu_3) + CH_3F(O) \rightarrow 2CH_3F(O) + 1048\ cm^{-1}$	$1.1\cdot10^{10}$	$1.5\cdot10^4$	207
$CH_3F(\nu_3) + Ar \rightarrow CH_3F(O) + Ar + 1048\ cm^{-1}$	$7.3\cdot10^8$	$2\cdot10^5$	207
$CH_3F(\nu_3) + He \rightarrow CH_3F(O) + He + 1048\ cm^{-1}$	$1.5\cdot10^{10}$	$1.7\cdot10^4$	207
$CH_3F(\nu_3) + CH_3F(\nu_3) \rightleftarrows CH_3F(2\nu_3) + CH_3F(O) + 10\ cm^{-1}$	$2.2\cdot10^{13}$	7	208
$CH_3F(3\nu_3) + CH_3F(O) \rightleftarrows CH_3F(O) + CH_3F(\nu_{1,4}) + 120{,}100\ cm^{-1}$	$2.2\cdot10^{12}$	70	208
$CH_3F(\nu_{1,4}) + CH_3F(O) \rightleftarrows CH_3F(O) + CH_3F(2\nu_{2,5}) + 10\ cm^{-1}$	$>1.7\cdot10^{13}$	<10	208
$CH_3F(2\nu_{2,5}) + CH_3F(O) \rightleftarrows 2CH_3F(\nu_{2,5}) + 10\ cm^{-1}$	$>3.3\cdot10^{12}$	<50	208
$CH_3F(\nu_3) + CH_3F(O) \rightleftarrows CH_3F(O) + CH_3F(\nu_6) - 133\ cm^{-1}$	$1.0\cdot10^{12}$	150	208
$CH_3F(\nu_3) + Ar \rightleftarrows CH_3F(\nu_6) + Ar + 133\ cm^{-1}$	$7.5\cdot10^{10}$	$2.2\cdot10^3$	195
$^{12}CH_3F(\nu_3) + {}^{13}CH_3F(O) \rightleftarrows {}^{12}CH_3F(O) + {}^{13}CH_3F(\nu_3) + 12\ cm^{-1}$	$1.7\cdot10^{13}$	10	196
	$2.8\cdot10^{13}$	6	194
$o\text{-}CH_3F(\nu_3) + n\text{-}CH_3F(O) \rightleftarrows o\text{-}CH_3F(O) + n\text{-}CH_3F(\nu_3)$	$3.5\cdot10^{13}$	5	196

excited state. Hence it follows that the simplest type of non-equilibrium in vibrational excitation may be a "discrepancy" between the vibrational and translational temperatures. This discrepancy may arise at low pressures under the conditions of continuous irradiation or at higher pressures under the conditions of pulsed irradiation. It is noteworthy that the rate of relaxation of the vibrational energy is determined by the deactivation of the lowest vibrational level only under the conditions of comparatively weak optical pumping. *V*–*T* relaxation processes involving higher vibrational levels, the rates of which is higher than that of relaxation involving the lowest level, play an appreciable role at high concentrations of vibrationally excited molecules[209].

The *V*–*V* relaxation processes are much faster, usually requiring between 10 and 100 collisions. For this reason it is much more difficult to achieve the vibrational "heating" of a specified degree of freedom, particularly since intramolecular vibrational energy transfer processes, occurring over periods shorter than the period between collisions, are possible in complex molecules[210]. The transfer of vibrational energy between isotopic molecules, involving virtually a resonance mechanism, is even faster than the collision processes involved in *V*–*V* relaxation. Less than ten collisions are required for this purpose[192–196].

Whereas the *V*–*T* relaxation of vibrationally excited molecules by inert gas molecules and atoms is comparatively slow, the rate of the *V*–*T* relaxation by free atoms is much higher and approaches the rate of the *V*–*V* processes. A large number of direct experimental measurements of the rate constants for these processes have been made in recent years; some of these have been examined in reviews[105,189,211]. The results of some of the latest measurements of the rate constants for the above processes are presented in Table 2. Comparison of the rate constants for the *V*–*T* relaxation of vibrationally excited molecules by inert gas molecules and atoms with the constants for relaxation by chemically active atoms showed that the rates of the latter are greater by 2–3 orders of magnitude. This implies that in real reacting systems, where the relative concentrations of atoms may exceed 10^{-3}–10^{-2} (for example, in flash photolysis or in processes occurring in an electric discharge), the relaxation of vibrationally excited molecules at such species must be taken into account.

VI. REACTIONS OF VIBRATIONALLY EXCITED MOLECULES IN THE CONDENSED PHASE AND ON THE SURFACES

Whereas in the gas phase superequilibrium concentrations of vibrationally excited molecules may be obtained at low temperatures even under the influence of the emission of continuous infrared lasers of comparatively low power (watts per cm^2), on passing to a condensed phase this requires a much greater radiation density—megawatts and gigawatts per cm^2.[31,212] Such radiation densities are attainable only in pulsed lasers. Furthermore, when energy with such a high density is incident on a given substance, considerable heating, leading to its evaporation, is inevitable. For example, it has been shown[213] that the interaction of the radiation from a pulsed CO_2 laser (energy per pulse 1 J, duration of pulse 80 ns) with water and chloroform leads to the formation of a shock wave as a result of the rapid evaporation of the liquid and the increase of pressure over the surface. Such interactions of infrared radiation with a given substance are undoubtedly of chemical interest. An apparatus has been described[214] for the synthesis of organometallic compounds by the interaction between the metals evaporated by the laser beam and the vapours of organic compounds. However, the discussion of processes beginning with a change in the phase state of the relevant substance under the influence of infrared radiation is outside the scope of the present review.

In view of the experimental difficulties mentioned above, the number of studies on the infrared photochemistry of the condensed phase is much smaller than the number of corresponding studies in the gas phase. The effect of the emission of a CO_2 laser on adenosine triphosphate and ammonium pyrophosphate, prepared in the form of potassium bromide discs, has been studied[215]. It was established that, after exposure to the pulsed radiation (with pulses lasting 100 ns), molecular structure are produced with an increased angle between the P–O–P bonds, while quasi-continuous irradiation (with pulses lasting 0.1–1 s) causes the same changes as thermal heating. A displacement of the complex-formation equilibrium under the influence of the pulsed radiation of a CO_2 laser incident on the interface between aqueous and organic uranyl nitrate solutions has been observed[216,217].

The above reactions are most likely to be due to the purely thermal effect of the laser emission, since the *V*–*T* relaxation times under these conditions should be short. Experiments at low temperatures, where the rates of the relaxation processes may be greatly reduced, are therefore more promising. For example, a study of the infrared fluorescence of the CO molecule in solid argon and neon matrices at 10–30 K established that, after the excitation of the $^{12}C^{16}O$ molecule to its lowest excited vibrational level by the second harmonic of the radiation from a pulsed CO_2 laser, signals appear due to the fluorescence of $^{12}C^{16}O$, $^{13}C^{16}O$, and $^{12}C^{18}O$ molecules in vibrational states up to $v = 8$.[218] The times during which the corresponding signals increase, determined by the rate of the *V*–*V* relaxation of CO, amounted to tens and hundreds of microseconds in these experiments (depending on the degree of dilution of CO by argon or neon), while the times during which the signal intensities decrease, determined by the rate of the *V*–*T* relaxation of the vibrationally excited CO molecules at Ar and Ne species and the emission of radiation, amounted to 15–20 ms. The comparatively low rates of relaxation in low-temperature matrices suggest that the effect of infrared laser emissions on such systems may exhibit a high isotopic and stereochemical selectivity. The behaviour of iron tetracarbonyl $Fe(CO)_4$, isolated in a methane matrix at 20 K, has been investigated[219]. $Fe(CO)_4$ was obtained by the ultraviolet irradiation of the matrix containing $Fe(CO)_5$. Heating to 35 K led to the regeneration of the pentacarbonyl; black body infrared emission (Nernst glower) induced the reaction $Fe(CO)_4 + CH_4 \rightarrow [Fe(CO)_4.CH_4]$, which does not occur when the matrix is heated. The influence of the radiation from a continuous CO laser (power 400–650 mW, intensity <1 W cm^{-2}) on $Fe(CO)_4$ enriched in carbon-13 (34%) initiated the same reaction but, depending on the radiation frequency, only isomers with a specific number and distribution of ^{13}CO groups reacted.

Isotopically selective dissociation of SF_6 in a low-temperature matrix under the influence of the pulsed radiation of a CO_2 laser has been observed[220]. Isotopically-selective evaporation of BCl_3, on irradiation by a continuous CO_2 laser of a film obtained by freezing boron trichloride at 77 K on a solid support, has been reported[221].

The study of the role of vibrational excitation in heterogeneous-catalytic reactions is of great interest. Such processes may be investigated at gas pressures which are sufficiently low to enable the vibrationally excited molecules generated by the laser emission in the bulk phase to reach the surface without losing vibrational energy by collisions. The influence of the vibrational excitation of N_2O molecules, due to the radiation from a continuous electric-discharge N_2O laser (with a power up to 90 mW) in the reaction $N_2O + Cu \rightarrow N_2 + CuO$ at pressures of approximately 1 mmHg, has been investigated[222] and it has been established that the probability of the reaction increases as a result of vibrational excitation by a factor of 5×10^3 (from 2.9×10^{-11} to 1.5×10^{-7}). This cannot be explained solely in terms of the reactivity of the vibrationally excited state of the N_2O (001) molecule with an energy of approximately 3 kcal mole^{-1}. An increase of reaction probability by a factor greater than $\exp(h\nu/RT)$, which does not exceed 60 at the experimental temperature (363 K), is impossible under these conditions. It appears that under the given experimental conditions higher vibrationally excited states are also populated, i.e. N_2O undergoes vibrational "heating" to a temperature greatly exceeding the translational temperature. Analogous studies were made in another investigation[223], where the stimulation of the heterogeneous ammonia decomposition reaction on the surface of platinum by the radiation from a CO_2 laser was observed.

Adsorption processes involving vibrationally excited molecules generated by continuous infrared radiation have been investigated in a number of studies[224-226]. The recorded isotope effects in the adsorption of BCl_3 and when the latter is filtered through finely dispersed sodium chloride exceed the equilibrium isotope effects.

Table 3. Characteristics of the infrared lasers used in photochemical research (studies on relaxation are not included).

Type of laser	Range of generation, cm^{-1}	Energy of quantum, kcal mole^{-1}	Power, W	Energy of pulse, J	Duration of pulse, s	Number of published studies
CO_2 *	900—1100	2.6—3.1	to 650	—	—	70
CO_2	900—1100	2.6—3.1	—	to 10	$3 \cdot 10^{-8}$—$1 \cdot 10^{-6}$	66
CO *	1500—2000	4.3—5.7	3,0	—	—	2
N_2O *	900—970	2.6—2.8	0,09	—	—	1
HF *	3500—3800	9.5—11.0	90	—	—	1
HCl	2500—2900	7.2—8.6	—	0.01	10^{-6}—10^{-5}	3
Neodymium	9400	27.0	—	to 10	10^{-3}	1
Neodymium + H_2SRS	1100—1200	3.2—3.5	—	0.5	$2 \cdot 10^{-8}$	1
Ruby + N_2 SRS	2330	6.7	—	0.8—1.4	$3 \cdot 10^{-8}$	1
Parametric $LiNbO_3$ oscillator	2800—18 300	8.2—52.9	—	10^{-5}	10^{-7}	1

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* Continuous operating conditions; pulsed conditions were employed in the remaining instances.

In conclusion we may note that the scope for the formulation and interpretation of laser-chemical studies in the condensed phase is significantly restricted by the scarcity of experimental data for vibrational relaxation under these conditions.

VII. CONCLUSION

Numerous experimental studies published in recent years are evidence for the vigorous development of infrared laser photochemistry. A characteristic feature of the initial stage of the development of this research field was a distinctly applied bias of many of the investigations, associated with the prospect of developing new isotope separation methods. The considerable possibilities of infrared lasers in carrying out selective chemical processes were demonstrated and the difficulties and unsolved problems arising in this connection were described. The proportion of studies directed to the solution of fundamental chemical kinetic problems has begun to increase in recent years: the characteristics of reactions under non-equilibrium conditions, the influence of various forms of energy on reactivity, the competition between the reaction and relaxation, and others.

The development of infrared photochemistry will undoubtedly depend on the progress in laser engineering. Analysis of published studies (Table 3) shows that most of them have been carried out with the aid of pulsed and continuous CO_2 lasers. The lack of commercial infrared lasers operating in other frequency ranges restricts the range of systems susceptible to experimental photochemical investigation. This restriction arises not only because the spectra of many molecules lack absorption lines falling within the range of CO_2 lasers but also because of the small energy of the emitted quanta of such lasers, which hinders the competition between the radiation-induced and thermal processes involving the generation of vibrationally excited molecules. Another factor which narrows the range of systems suitable for experimental study is the difficulty of a smooth adjustment of the infrared frequency of lasers. However, these difficulties are not insurmountable, since tunable lasers, covering virtually the entire infrared range (at least in the pulsed version), already exist in physics laboratories. One may hope that the use of this new laser technique will promote the successful development of infrared photochemistry.

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Long-range Tunnelling Electron Transfer in Chemical Reactions

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We have generalised recent experimental and theoretical results on a process which is uncommon in classical chemistry: long-range tunnelling electron transfer. These reactions play an important role in various areas of chemistry and biochemistry, and they offer new pathways for controlling the direction of chemical change. 94 references.

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I. INTRODUCTION

It has long been thought self-evident that bimolecular reactions can occur only when the interacting molecules are in direct contact, i.e. when the approach distance is equal to the sum of the gas-kinetic or crystallographic radii. However several reactions between particles separated by much larger distances (up to many tens of Ångstroms) have recently been discovered. The reacting species are separated either by molecules of the medium (condensed phase) or by a vacuum (gas phase).

These are the so-called tunnelling (or sub-barrier) long-range electron transfer reactions. During these reactions an electron passes (tunnels) through the energy barrier separating the reactants, which can be much higher than the intrinsic energy of the electron (several electron-volts). These transitions contravene the rules of classical mechanics, but they are permitted in quantum mechanics.

The quantum-mechanical tunnelling of particles through potential barriers was first postulated in physics to explain the ionisation of atoms in a strong electric field[1], the cold emission of electrons from metals[2], and the α-decomposition of atomic nuclei[3,4]. A simple formula was obtained[3] for the transition probability w per unit time of a particle of energy E below a potential barrier of height $U(x)$:

$$w = \nu_0 \exp\left(-\frac{2}{\hbar}\int_0^r |p|\,\mathrm{d}x\right). \tag{1}$$

In this formula ν_0 is the collision frequency of the particle with the potential barrier, $p = \{2m[U(x) - E]\}^{1/2}$, m is the mass of the particle, and $\hbar$ is Planck's constant. Eqn. (1) can be written more simply

$$w = \nu_0 \exp(-2r/a), \tag{2}$$

where $a = \gamma\hbar/[2m(U_{\max} - E)]^{1/2}$, $U_{\max}$ is the maximum value of $U(x)$ (the barrier height), $\gamma \simeq 1$ is a numerical coefficient depending on the shape of the barrier, and the distance r corresponds to the width of the barrier (see Fig. 1). It is evident from formula (2) that the probability of the tunnelling transition decreases exponentially as the mass of the particle increases. Hence the most effective tunnelling transitions can be expected in reactions involving the lightest of all chemical particles: the electron.

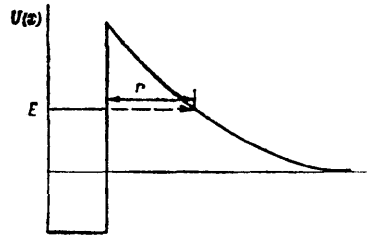

Figure 1. Tunnelling electron transfer through an energy barrier.

There have been many attempts to estimate the maximum distance through which an electron can tunnel in chemical reactions[5,6] (see also Ref. 7). All these calculations were based on formula (2), assuming a frequency ν_0 equal to the characteristic frequency of the motion of electrons in atoms ($\nu_0 \simeq 10^{15}-10^{16}$ s^{-1}), and a barrier height $U_{\max}$ equal to the ionisation potential of the donor particle. These estimates are too approximate to confirm or deny with any reliability the hypothesis of long-range tunnelling transitions of electrons in chemical reactions. Their most serious shortcoming is that formula (2) was obtained for processes in which the particles can tunnel into a region of space possessing a continuous spectrum of energies: strictly speaking, this formula is not applicable to chemical reactions, in which the electron is transferred between states with discrete energy levels. Hence the concept of long-range electron transfer in chemical reactions did not gain wide acceptance until direct experimental evidence of the reality of this process became available.

The most convincing evidence of long-range electron tunnelling was obtained in studies of the low-temperature oxidation and reduction of solids. Typical of these processes are the reactions of trapped electrons (e_{tr}^-) with various acceptors (organic or inorganic molecules, ions, ion-radicals, and transition metal complexes). The rates of many of these reactions were found to be temperature-independent and much higher than the rate of diffusion-limited collisions between reactants.

Examples of long-range electron transfer reactions in the liquid phase include the reaction of hydrated electrons (e_{aq}^-) with various inorganic anions (CrO_4^{2-}, MnO_4^-, etc.) in dilute solutions. The effect of the electrostatic repulsion between like charges on the rate of these reactions is abnormally low, suggesting a large separation between the charges at the moment of reaction.

Typical gas-phase reactions involving a long-range electron transfer step are the reactions between alkali metal atoms and halogen molecules, for example

$$K + I_2 \rightarrow K^+ + I_2^- \rightarrow KI + I.$$

Measurements by the molecular beam method have shown that the interaction radii for these reactions can exceed the gas-kinetic radii by a factor of two.

II. HISTORICAL ACCOUNT OF THE DISCOVERY AND STUDY OF LONG-RANGE TUNNELLING ELECTRON TRANSFER REACTIONS

The reactions of alkali metal atoms with halogen molecules in the gas phase are the first reported example of chemical reactions at long range. Reaction cross-sections somewhat greater than the gas-kinetic cross-sections were observed in a study[8] of diffusion flames published in 1932. The correctness of this observation was confirmed by later, more precise measurements by the molecular beam method[9-11] carried out in the 1950's and 1960's. The following mechanism was proposed[12]: initially the reactants approach to within a distance such that the difference between the ionisation potential I_M of the metal atom and the electron affinity A_{X_2} of the halogen molecule is equal to the energy of the interacting unit charges, i.e.

$$I_M - A_{X_2} = e^2/r_c. \tag{3}$$

At this instant the electron passes under the barrier from M to X_2. Immediately after the electron transfer the long-range Coulombic forces between M^+ and X_2^- begin to operate, making the particles approach each other until the ordinary chemical forces can break the X–X bond and form an M–X bond.

Table 1. Interaction radii r_e, distances r_c,[10] and sums of gas-kinetic radii of the reactants $r_M + r_{I_2}$ for the reactions between alkali metals and iodine (Na* is an excited sodium atom).

M	r_e, Å	r_c, Å	$r_M + r_{I_2}$, Å
K	6.3	5.26	4.2
Pb	7.3	5.63	4.4
Cs	7.6	6.43	4.6
Na	7.9	4.07	3.8
Na *	8.2	—	3.8

The interaction radii r_e calculated from the measured cross-sections for a series of reactions are compared in Table 1 with the distances r_c calculated by formula (3) and with the sums of the gas-kinetic radii of the reactants $r_M + r_{X_2}$. It can be seen that both r_e and r_c are greater than $r_M + r_{X_2}$, i.e. the electron transfer step occurs at distances beyond the range of chemical (exchange) forces.

The next important step was the discovery[13-16] of anomalously large rate constants for the diffusion-controlled reactions of hydrated electrons with various inorganic anions in aqueous solutions. Table 2 lists the highest observed rate constants (k_e) for reactions between e_{aq}^- and inorganic anions and cations, and also the theoretical diffusion-limited rate constants (k_D) for the same reactions, calculated by the Debye formula[17] from the known radii and diffusion coefficients of the reactants[16]

$$k_D = 0{,}004\pi ND\sigma\,(z_A e^2/\varepsilon kT\sigma)\,[\exp(z_A e^2/\varepsilon kT\sigma) - 1]^{-1}. \tag{4}$$

Table 2. Maximum reported values of the rate constants k_e and of the diffusion constants k_D for the reactions of e_{aq}^- with anions and cations[16] (en is ethylenediamine, EDTA is the ethylenediaminetetra-acetate ion).

Acceptor	$10^{10}k_e$, litre mole^{-1} s^{-1}	$10^{10}k_D$, litre mole^{-1} s^{-1}
$Co(NO_2)_6^{3-}$	3.2—5.8*	0.27
$Co(C_2O_4)_3^{3-}$	1.3	0.27
$Co(CN)_5Cl^{3-}$	1.8*	0.19
$Cr(C_2O_4)_3^{3-}$	1.8*	0.25
$Cr(EDTA)^-$	2.6*	1.2
$Cr_2O_7^{2-}$	3.3	0.53
CrO_4^{2-}	1.8	0.33
$Mn(CN)_6^{4-}$	0.54	0.068
$Fe(CN)_5NO^{2-}$	2.4	0.50
MnO_4^-	2.2	0.94
O^-	2.2	0.86
NO_3^-	0.85	0.52
$Co(NH_3)_6^{3+}$	8.2	9.2
$CO(NH_3)_5Br^{2+}$	6.2	6.2
$Co(en)_2CO_3^+$	4.9	4.4
$Cr(H_2O)_6^{3+}$	6.2	6.9
$Cr(NH_3)_5Cl^{2+}$	6.2	6.4
$Cr(en)_3^{3+}$	7.8	9.2
$Cr(en)_2(NCS)_2^+$	4.2	4.4
$Os(NH_3)_6^{3+}$	7.2	8.9
$Rh(NH_3)_6^{3+}$	7.9	8.9

*Experimental value; the k_e values for all the other acceptors in the Table are extrapolated to zero ionic strength in the solution.

In this formula $z_A e$ is the charge on the acceptor, $D = D_A + D_e$ refers to the diffusion coefficients of the acceptor and of e_{aq}^-, σ is the distance between the reactants at the instant of electron transfer, $\epsilon = 81$ is the dielectric constant of water, N is Avogadro's number, k is Boltzmann's constant, and T is the temperature. In the calculation of k_D it was assumed that electron transfer occurs by direct collision between the reactants i.e. that $\sigma = r_A + r_e$ where r_A and r_e are the radii of the reactants. It is clear from Table 2 that the largest values of k_e for the reactions of e_{aq}^- with anions are similar to the k_e values for the reactions of e_{aq}^- with cations, and much greater than the k_D constants calculated by formula (4). The relative insensitivity to electrostatic repulsion effects of the rate of the reaction of e_{aq}^- with anions was taken as evidence that fast reactions of this type take place at distances in excess of the sum of the radii of the reactants.

Nevertheless the experimental evidence for long-range electron transfer in liquids and gases was too limited for a wide recognition of the importance of long-range interactions in chemistry. In view of the complexity of the molecular beam method, the observed difference between the interaction radii and the sum of the gas-kinetic radii ($r_M + r_{X_2}$) did not seem unduly large for the gas-phase reactions examined. In the reactions of e_{aq}^- with anions a weak electrostatic repulsion effect on the rate of the association of charged particles with their counter-ions could not be totally excluded.

Decisive proof of the existence of long-range tunnelling electron transfer processes was obtained only recently, from studies of oxidation–reduction reactions in solid matrices at low temperatures, i.e. under conditions where the diffusion of reactants and their mutual approach to within short distances can be rigorously excluded. Under these conditions long-range tunnelling electron transfer becomes the only possible mechanism for the reaction, and it can be observed and investigated unambiguously.

In 1965 it was found[18] that the trapped electrons (e_{tr}^-) formed by the γ-radiolysis of 2-methyltetrahydrofuran (2-MTHF) disappear slowly at 77 K. The decay of the e_{tr}^- species was ascribed[19] to a tunnelling reaction with hole centres, and a tunnel mechanism was proposed[20] for the disappearance of e_{tr}^- in an aqueous alkali glass containing additives. The Gamow formula (2) has been used[19,21] to calculate the distances to which electrons can tunnel in low-temperature radiation-chemical reactions (several tens of Ångstroms).

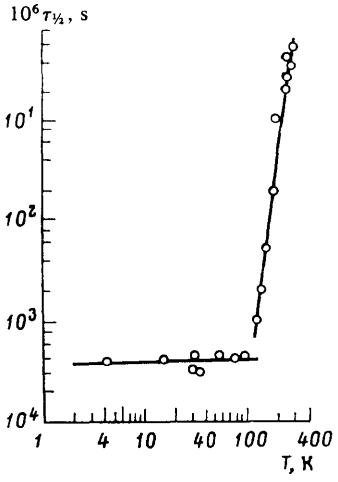

Figure 2. Characteristic time $\tau_{1/2}$ against temperature for the transfer of an electron from the reduced form of cytochrome *c* to the oxidised form of chlorophyll in *Chromatium D* bacteria.

However none of these results[18-20] definitely excluded the possibility of a diffusional mechanism for the disappearance of e_{tr}^-, or of a reaction with acceptors in direct contact with the trapped charge. Furthermore the use of Gamow's formula raises some objections (as was pointed out above). Nevertheless the work[19-21] stimulated further research in this area.

The first definitive formulation of the importance of tunnelling processes appeared in a paper by Chance and DeVault[22], who studied the temperature dependence of the characteristic time $\tau_{1/2}$ for the transfer of electrons from the reduced form of cytochrome *c* to the oxidised form of chlorophyll in *Chromatium D* bacteria over a wide range of temperature (300–4.2 K). They found a normal Arrhenius dependence at the higher temperatures ($T > 130$ K), but at $T < 130$ K $\tau_{1/2}$ was independent of temperature (see Fig. 2). Hence a diffusion-limited mechanism could be rigorously excluded, at least at $T < 130$ K. A detailed theoretical analysis of the electron transfer process in this system is given in a later paper[23]. However, as before, direct contact between the active centres of cytochrome *c* and those of chlorophyll in the bacteria at the instant of reaction could not be entirely excluded.

A tunnel mechanism for the electron transfer process was proposed also to explain[24-26] the temperature-independent luminescence produced by electron–hole recombination in γ-irradiated alkali halide crystals. The model[27,28] proposed to explain similar effects assumes that the recombination of donor–acceptor pairs in semiconductors also takes place by a tunnel mechanism. However the distance to which the electron is transferred in real systems was, again, unknown.

The first direct experimental demonstration[29] of a reaction between donors and acceptors a large distance apart was the reaction between e_{tr}^- and the anion-radical O^-. Both particles are formed, in equal yield, by the low-temperature radiolysis of frozen aqueous alkaline solutions, and they can be monitored through their characteristic optical (e_{tr}^-) and ESR (e_{tr}^- and O^-) spectra. It was possible to show from the width of the ESR spectral line that the distance between the reacting particles could not be less than 20 Å for most of the reacting pairs[30]. Also, the e_{tr}^- and O^- species were found to decay at the same rate even at very low temperatures. The kinetic curves for different temperatures are indistinguishable within experimental error over a wide range of time (five orders of magnitude), and they are linearised in an unusual set of coordinates (concentration against logarithm of time, see Fig. 3). A diffusion-limited mechanism for this process is excluded by the coincidence of the kinetic curves for different temperatures, and the distance between the reactants confirms the reality of the long-range electron transfer process. The unusual type of kinetic equation was simply explained by the distribution of distances $e_{tr}^- \ldots O^-$ between the reacting pairs (see below).

Temperature-independent kinetics (at T = 77.66 and 4.2 K) were reported shortly afterwards[31] for the luminescence quenching process involving the recombination of e_{tr}^- with a biphenyl cation in a methylcyclohexane glass.

A detailed analysis[32] of the effect of added acceptors on the yield of ionic radiolysis products (e_{tr}^- and anion-radicals) revealed satisfactory agreement with the tunnelling electron transfer mechanism for the formation and disappearance of these particles. In particular it was found that the disappearance of e_{tr}^- in 2-MTHF doped with naphthalene (Nh) is accompanied by the formation of the Nh^- anion-radical in corresponding amounts (by the reaction $e_{tr}^- + Nh \rightarrow Nh^-$). The kinetic curves for this reaction at 77 and 87 K were indistinguishable.

Because of the logarithmic time-dependence of the concentration of reactants quantitative kinetic studies of tunnelling electron transfer reactions in solid matrices must extend over very long periods. For example, the reaction between e_{tr}^- and O^- had to be monitored over 5 orders of magnitude of time (see Fig. 3). Hence the development of pulsed techniques for measuring the kinetics of low-temperature reactions between active intermediates in radiolysis over many orders of magnitude, including very short times (from 10^{-6} to 10^2 s), has played a very important role in subsequent studies of tunnelling electron transfer reactions[32]. Pulsed apparatus has been used to measure the kinetics of the reaction of e^-_{tr} with many different acceptors[32,33]. By combining measurements made in this apparatus with more traditional measurements over long periods the kinetics of the reaction

$$e^-_{tr} + Cu\,(en)_2^{2+} \rightarrow Cu\,(en)_2^{+} \qquad (5)$$

(where en is ethylenediamine) have been studied quantitatively over time intervals between 10^{-6} and 10^6 s.[34,58]

The next important stage in the study of long-range electron transfer reactions was the development of special kinetic equations[35-47], including equations for paired[35,39,46], random[37-39], and arbitrary[35,36,46] distributions of reactants in the absence of diffusion, and also in the presence of diffusion for a random[40-42,44] or an arbitrary[43,45,47] distribution of reactants. It was shown that these equations give an accurate description of the observed kinetics of tunnelling reactions over the whole range of reaction times[58]. As an example we show in Fig. 4 the experimental (points) and the theoretical (lines) kinetic curves for the reaction between e^-_{tr} and $Cu(en)_2^{2+}$ at different concentration of $Cu(en)_2^{2+}$. This agreement between theory and experiment provides an important confirmation of the tunnel mechanism of the reaction.

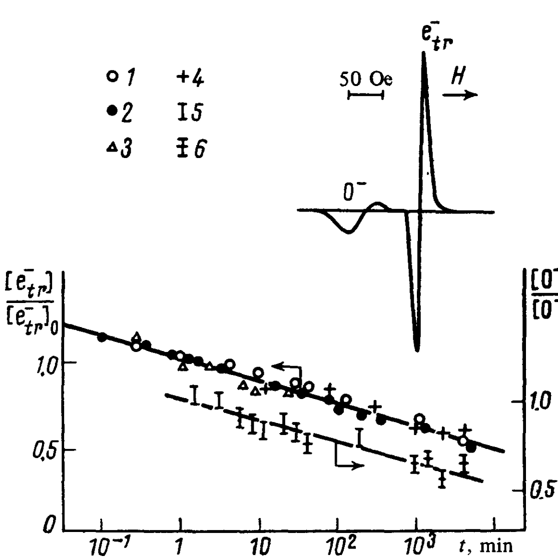

Figure 3. ESR spectra and decay curves for e^-_{tr} and O^- in 10 *M* aqueous NaOH; $[e^-_{tr}]_0$ and $[O^-]_0$ are the concentrations at $t_0 = 1$ min; *1*), *2*), *3*), and *5*) β-radiolysis, *4*) and *6*) γ-radiolysis; *D* values *1*) 3×10^{19}, *2*) 3.6×10^{20}, *3*)–*6*) 1.2×10^{20} eV cm^{-3}; *1*), *2*), *5*), *6*) 77 K, *3*) 120 K, *4*) samples stored at 4.2 K but irradiated and measured at 77 K.

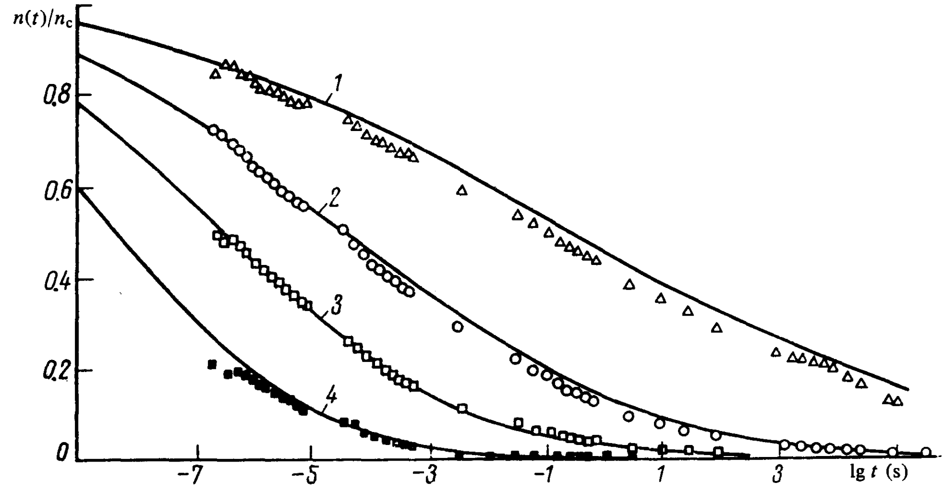

Figure 4. Kinetic curves for the reaction between e^-_{tr} and $Cu(en)_2^{2+}$ in 10 *M* aqueous NaOH solution at 77 K for different concentrations of $Cu(en)_2^{2+}$: *1*) 0.005, *2*) 0.01, *3*) 0.05, *4*) 0.1 *M*. The points are experimental, the curves are theoretical calculations by Eqn. (26) with the values $\nu = 10^{15.2}$ s^{-1} and $a = 1.83$ Å.

As long as long-range electron transfer had been observed only in the low-temperature reactions of e^-_{tr} there remained a doubt that the mechanism could be specific for this particle only, and that an alternative explanation could be delocalisation of e^-_{tr} (as in the case of polarons) over a large number of centres in solid matrices. Therefore the discovery of charge transfer over large distances in the low-temperature reactions of ordinary chemical species (inorganic anion-radicals and transition metal compounds) was the next important step[48,49]:

$$O^- + Fe(CN)_6^{4-} \rightarrow O^{2-} + Fe(CN)_6^{3-}, \qquad (6)$$

$$SO_4^- + FeSO_4 \rightarrow SO_4^{2-} + FeSO_4^+, \qquad (7a)$$

$$SO_4^- + AgNO_3 \rightarrow SO_4^{2-} + AgNO_3^+. \qquad (7b)$$

The list of reactions of this type grew rapidly, and it now includes electron transfer processes from inorganic anion-radicals to organic molecules[50,51], from electronically excited molecules to various acceptors[52-54], between compounds of metals of variable valency[49,55], and from F-centres to hole centres in crystals[56] (see also Refs. 24-26).

The logical extension of this work was a quantitative analysis of the accumulated kinetic data[57,58] and a detailed theoretical discussion of the mechanism of the elementary act of the long-range tunnelling electron transfer process in solids[23,58-60].

Thus significant progress has been made in the study of long-range tunnelling electron transfer reactions. In this review we shall examine the theory of these processes, and we shall analyse existing kinetic data uniquely from the standpoint of this theory.

III. MODELS OF THE ELEMENTARY ACT OF LONG-RANGE ELECTRON TRANSFER

The simplest model used to describe long-range electron transfer reactions involves the tunnelling of an electron from a potential well through an energy barrier $U(x)$ (see Fig. 1). This model leads to formulae (1) and (2) for the variation of the transition probability per unit time with distance. According to this model the frequency ν_0 in Eqn. (2) is the characteristic frequency of the motion of electrons in atoms, i.e. $\nu_0 \simeq 10^{16}$ s^{-1}. The model also assumes that the parameters ν_0 and a are fully determined by the initial state of the system, i.e. the properties of the electron donor and those of the medium, and are independent of the final state, i.e. the properties of the electron acceptor. However both these predictions of the model were found to be incompatible with experimental results, since both ν_0 and a in practice depend on the nature of both the donor and the acceptor. For example, ν_0 can vary from 10^6 to 10^{21} s^{-1} for different reactions[58] (see Tables 3 and 4. But in spite of these shortcomings of the model formula (2) in general gives a correct qualitative description of the variation of w with r.

More exact models of tunnelling electron transfer between particles A^- and B in a solid,

$$A^- + B \rightarrow A + B^- \qquad (8)$$

have been proposed[23,58-60]. The qualitative difference between these models and the previous model is the inclusion of the interaction (important in principle) between electronic and nuclear degrees of freedom in the molecules of the reactants and of the medium. As a result of this interaction the transition probability is substantially influenced by the motion of the nuclei of the reacting molecules and of the intervening molecules of the medium. Energy conservation is preserved by the transformation of the energy set free by the electron transfer into vibrational energy of the nuclei.

The newer models[23,58-60] differ in the type of nuclear motion assumed. Some workers[23,59,60] use the harmonic approximation to the vibration of the nuclei, whereas we have allowed for strong anharmonicity of the nuclear motion[58]. The model proposed in Ref. 58 gives a fuller physical description of long-range tunnelling electron transfer, and is fully consistent with all available experimental data. The transition probability of an electron per unit time is expressed as

$$w = \sum_i \sum_f p_i w_{if}\,. \qquad (9)$$

The summation is taken over all the initial (i) and the final (f) states of the nuclear motion. In this expression p_i is the probability of an initial state i of energy E_i:

$$p_i = e^{-E_i/kT} / \sum_i e^{-E_i/kT}, \qquad (10)$$

and w_{if} is the probability of a transition from the initial state i to the final state f. The variation of w_{if} with distance is given, as before, by the simple exponential function

$$w_{if} = \nu_{if} \exp(-2r/a_{if}). \qquad (11)$$

This dependence arises, as in the case of the simplest model of tunnelling, from the exponential damping of the electronic wave functions in a classically inaccessible region of space. The ν_{if} values for different i or f in formula (11) should be different, in general. The a_{if} values are identical for all states of nuclear motion corresponding to the same electronic energy level, and they can vary only as a result of a change in electronic state. Hence in transfer processes not involving excited states Eqn. (9) simplifies to a form identical to Eqn. (2), i.e.

$$w = \nu \exp(-2r/a), \qquad (12)$$

where $\nu = \sum\limits_i \sum\limits_f p_i \nu_{if}$.

However the parameters a_{if} and ν_{if} have a physical significance entirely different from that of the parameters a and ν_0 used in the simplest model. The parameter a is the half-sum of the Bohr radii of the electron in the initial (a_{A^-}) and the final (a_{B^-}) state in a medium of dielectric constant ϵ:

$$a = \frac{1}{2}(a_{A^-} + a_{B^-}), \qquad (13)$$

which can also be written

$$a = \frac{1}{2}\varepsilon^{1/2}(a^0_{A^-} + a^0_{B^-}), \qquad (14)$$

where $a^0_{A^-}$ and $a^0_{B^-}$ are the Bohr radii of the centres A^- and B^- in a vacuum. The subscripts i and f have been omitted in Eqns. (13) and (14). It can be seen from Eqn. (14) that the parameter a is symmetrically dependent on the properties of both the initial and the final state of the system, and also on the properties of the medium.

The parameter ν is a complex combination of the characteristics of electronic and nuclear motions in the system, and cannot be interpreted simply as the collision frequency of the electron with the potential barrier. According to our calculations ν can be vanishingly small under unfavourable conditions, and under favourable conditions it can exceed the characteristic frequency of the motion of electrons in atoms and be as high as 10^{22} s^{-1}.[58]

We note from Eqn. (9) that at low temperatures (when only the lowest initial state i is populated) the rate of an exothermic electron transfer reaction is independent of temperature:

$$w = \sum_f w_{0f}. \tag{15}$$

However at higher temperatures w can depend on T: depending on the relative probabilities of electron transfer from the ground state and from an excited state, w can either increase or decrease with increase of T.[58,61] The quantity

$$\tau = [w(r)]^{-1} = \nu^{-1}\exp(2r/a) \tag{16}$$

is the characteristic time for the tunnelling of the electron to a distance r. Eqn. (16) leads to the following expression for the average distance R_t to which the electron can tunnel in time τ:

$$R_t = (a/2)\ln \nu\tau. \tag{17}$$

Because of the exponential dependence of w on r the transition probability of the electron in time τ is almost unity for $r < R_t$ and close to zero for $r > R_t$.

IV. FORMAL KINETICS OF TUNNELLING ELECTRON TRANSFER REACTIONS

According to formula (12) the probability of a tunnelling transition for the electron decreases rapidly as the distance r between the reacting particles increases. In a typical situation (condensed medium) there is a distribution of the distance r between the reactants, leading to an unusual type of overall reaction kinetics: the variation of concentration $n(t)$ with time t is described by complex functions having $\lg t$ as their argument (see below). The specific form of these functions depends on the spatial distribution of the reactants and on the relative rates of tunnelling transitions and of diffusion.

A fruitful approach in the development of kinetic equations for tunnelling reactions was the use of equations for the normal concentrations of donors $n(r,t)$ and acceptors $N(r,t)$: the concentrations of donors $n_i(r,t)$ and acceptors $N_i(r,t)$ at a distance r from an arbitrarily chosen (i-th) acceptor (or donor) particle averaged at time t over the ensemble of particles of the opposite kind[62,63]:

$$n(r,t) = \sum_{i=1}^{N(t)} n_i(r,t), \tag{18}$$

$$N(r,t) = \sum_{i=1}^{n(t)} N_i(r,t). \tag{19}$$

In these expressions $n(t)$ and $N(t)$ are the volume average concentrations of donors and acceptors. The nominal and the volume average concentrations are related by the expressions[62]

$$n(t) = \lim_{r\to\infty} n(r,t), \tag{20a}$$

$$N(t) = \lim_{r\to\infty} N(r,t), \tag{20b}$$

$$n(t)\cdot N(r,t) = N(t)\cdot n(r,t), \tag{21}$$

$$n(0) - n(t) = N(0) - N(t), \tag{22}$$

where $n(0)$ and $N(0)$ are the average concentrations of donors and acceptors at zero time.

By assuming that each donor can react with an arbitrary acceptor, and that diffusional approach between the reactants can take place in parallel with the direct tunnelling transition, we arrive at the following equation for the nominal and the average concentrations as a function of time[45]

$$\frac{\partial}{\partial t}n(r,t) = -\left[w(r) + \int_0^\infty w(\rho)4\pi\rho^2 N(\rho,t)\,\mathrm{d}\rho\right]n(r,t) + \frac{D}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial n(r,t)}{\partial r}\right), \tag{23a}$$

$$\frac{\partial}{\partial t}N(r,t) = -\left[w(r) + \int_0^\infty w(\rho)4\pi\rho^2 n(\rho,t)\,\mathrm{d}\rho\right]N(r,t) + \frac{D}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial N(r,t)}{\partial r}\right), \tag{23b}$$

$$\frac{\mathrm{d}}{\mathrm{d}t}n(t) = -\int_0^\infty w(\rho)4\pi\rho^2 N(\rho,t)\,\mathrm{d}\rho\, n(t), \tag{24a}$$

$$\frac{\mathrm{d}}{\mathrm{d}t}N(t) = -\int_0^\infty w(\rho)4\pi\rho^2 n(\rho,t)\,\mathrm{d}\rho\, N(t). \tag{24b}$$

The general analytic solution of the system (23)–(24) is very cumbersome[45], but a much simpler solution is obtained by ignoring the diffusional mechanism:

$$\frac{n(t)}{n(0)} = \frac{1 - N(0)/n(0)}{1 - [N(0)/n(0)]\exp\left\{[1 - n(0)/N(0)]\int_0^t\int_0^\infty w(\rho)\exp[-w(\rho)t]\,N(\rho,0)\,4\pi\rho^2\,\mathrm{d}\rho\,\mathrm{d}t\right\}}. \tag{25}$$

For the most important case (in practice) of a random distribution of reactants, when $N(r,0) = N(0)$, we obtain from (12) and (25)

$$n(t)/n(0) = \exp[-(\pi a^3/6)N(0)\ln^3 \nu t] \tag{26}$$

in the case of $N(0) \gg n(0)$, and

$$n(t)/n(0) = [1 + n(0)(\pi a^3/6)\ln^3 \nu t]^{-1} \tag{27}$$

in the case of $N(0) = n(0)$.

The physical significance of Eqns. (26) and (27) is clear. The quantity $R_t = (a/2)\ln \nu t$ is the average distance to which the electron can tunnel in time t (see above). Hence the quantity $\exp[-(\pi a^3/6)N(0)\ln^3 \nu t] \equiv \exp[-(4\pi/3)N(0)R_t^3]$ in the right-hand side of Eqn. (26) is the probability of finding a donor particle outside the effective reaction volume $V_t = (4/3)\pi R_t^3$ surrounding an arbitrary acceptor particle, i.e. the probability that the particle will not disappear as a result of a tunnelling reaction at time t.

Eqn. (27) can be rewritten

$$1/n(t) - 1/n(0) = (4/3)\pi R_t^3. \tag{28}$$

This equation expresses the fact that the increase in time t of the mean volume associated with a single donor particle, $\Delta V = [n(t)]^{-1} - [n(0)]^{-1}$, is $(4/3)\pi R_t^3$.

Most experiments on the kinetics of tunnelling reactions have been made in glassy solutions, in which the spatial distribution of reactants was approximately random and the concentration of one of the reactants was usually much greater than that of the other. The results agree well with Eqn. (26), as shown by the experimental and the calculated kinetic curves for reaction (5) which are compared in Fig. 4. The calculated curves were obtained by Eqn. (26), the parameters a and ν being chosen so as to optimise the agreement between calculation and experiment. It is clear from Fig. 4 that the kinetics of reaction (5) can be described quantitatively over a wider range of time (12 orders of magnitude) and at concentrations $N(0) = 0.1$–0.01 M $\mathrm{Cu(en)}_2^{2+}$ by selecting only two parameters. This means that Eqn. (26) correctly describes the quantitative dependence of the concentration $n(t)$ both on time t and on the concentration of the other reactant $N(0)$. The optimum values of the parameters ($a_{\text{opt}} = 1.83$ Å and $\nu_{\text{opt}} = 10^{15\cdot 2}$ s^{-1}) are entirely reasonable in the light of other theoretical considerations.

Another practically important case is that of a paired distribution of reactants. Kinetic equations for tunnelling reactions between isolated donor–acceptor pairs cannot be obtained from Eqns. (23) and (24) because the concept of a nominal concentration is meaningless for isolated pairs. Kinetic equations for the tunnelling recombination of isolated pairs were obtained[29] by assuming a rectangular distribution of the pairs with respect to distance r, and also by assuming an arbitrary distribution[35].

If the distribution of the pairs in distance is described by the function $f(r)$ the change with time of the number $dn(t)$ of pairs separated by a distance between r and $r + dr$ is given by

$$\frac{\delta}{\delta t}[dn(t)] = -w(r) \cdot dn(t). \tag{29}$$

Integrating Eqn. (29) with respect to time and using the initial condition $dn(0) = n(0)\cdot f(r)\cdot dr$ (where $n(0)$ is the total number of pairs at $t = 0$) we obtain

$$dn(t) = n(0)\exp[-w(r)t] \cdot f(r) \cdot dr. \tag{30}$$

Integration of Eqn. (30) with respect to r gives an expression for the time-change of the number of donor–acceptor pairs $n(t)$:

$$n(t)/n(0) = \int_0^\infty \exp[-w(r)t] \cdot f(r) \cdot dr. \tag{31}$$

For a rectangular distribution of the pair separations we have

$$f(r) = \begin{cases} (r_{\max} - r_{\min})^{-1} & \text{for} \quad r_{\min} \leqslant r \leqslant r_{\max}, \\ 0 & \text{for} \quad r > r_{\max}; \ r < r_{\min}. \end{cases} \tag{32}$$

Under the conditions $\ln \nu t \gg 1$ and $r_{\max} \gg R_t \gg r_{\min}$ we obtain from Eqns. (32) and (31)

$$n(t)/n(0) = [r_{\max} - (a/2)\ln(\nu t)]/(r_{\max} - r_{\min}). \tag{33}$$

Like Eqns. (26) and (27), Eqn. (33) has a clear physical meaning. It expresses the fact that for a rectangular distribution in r the fraction of the particles which do not undergo recombination at time t is $(r_{\max} - R_t)/(r_{\max} - r_{\min})$.

As shown in Fig. 3, Eqn. (33) accurately describes the kinetics of the recombination of the e_{tr}^- and O^- particles formed in equal yield during the radiolysis of aqueous alkaline glasses.

1. Effect of an Electric Field on the Kinetics of Tunnelling Recombination

Formula (12) applies for an isotropic configuration of the function $w(r)$. However $w(r)$ can become anisotropic in the presence of an electric field: the energy barrier opposing electron transfer is raised in the direction of the field and lowered in the opposite direction. Under these conditions the parameter a in Eqn. (12) is smaller for transfer in the direction of the field than in the opposite direction. In principle the parameter ν also can be altered by the shift in the energy levels of the initial and the final state produced by the application of the field. However, in practice, we only need to be concerned with the effect of the field on the parameter a. The following formula for the transition probability in a constant electric field E has been proposed[46] to replace Eqn. (12) when the parameter a is asymmetric:

$$w(r) = \nu \exp[(2r/a_0) - (r^2 eE\cos\theta)/(2a_0V_0)], \tag{34}$$

where a_0 is the value of a in the absence of the field, e is the electronic charge, θ is the angle between the direction of electron transfer and that of the field, and V_0 is a parameter which characterises the binding energy of the electron to the centres A and B. In the derivation of Eqn. (34) it is assumed that the change in the interaction energy of the electron with the electric field produced by the transfer from the donor to the acceptor is small in comparison with V_0.

By inserting Eqn. (34) into (25) or (31) we obtain kinetic equations for tunnelling reactions in the presence of a field. In this way expressions were obtained[46] for the change with time of the luminescence intensity produced by the tunnelling recombination of donors and acceptors in paired

$$I(t) = A\{f[(a_0/2)\ln(\nu t)]/4\ln b\} \cdot (1/x\tau) \cdot \ln[(1 + bx)/(1 + x/b)] \tag{35}$$

or in unpaired arbitrary distributions

$$I(t) = AN[(a_0/2) \cdot \ln(\nu t), 0] \cdot (\pi a_0^3/2x\tau) \cdot [\ln^2(\nu\tau)/2\ln b] \times \\ \times \ln[(1 + bx)/(1 + x/b)] \cdot [n(t)/n(0)] \cdot [N(t)/N(0)]. \tag{36}$$

In these expressions (which apply for $t > \tau$) the parameter τ is the time between the beginning of the tunnelling reaction and the application of the electric field, $f(r)$ is the initial distribution function of the distance between particles in a pair, $N(r, 0)$ is the initial arbitrary concentration of acceptors, $x = (t - \tau)/\tau$, and

$$b = \exp[(a_0Ee/8V_0)\ln^2(\nu t)].$$

It can be seen from Eqns. (35) and (36) that the kinetics of luminescence quenching by the application of a field are entirely determined by the spatial distribution of the reactants and by the parameter b, which can be evaluated from the discontinuous change in luminescence intensity at the instant when the field is applied[46].

Eqn. (35) has been used[46] to analyse results[64] on the influence of a field on the quenching kinetics of the luminescence due to the paired tunnelling recombination of e_{tr}^- with its counter-ion (the cation of tetramethyl-p-phenylenediamine) in glassy 3-methylpentane. The distribution function of the electron to counter-ion distances found in this way.

2. Kinetic Equations for Tunnelling Reactions in the Presence of Diffusion of Reactants

Diffusion can influence the kinetics of these reactions because it affects the spatial distribution of the reactants.

A general solution of the system of equations (23)–(24) has been obtained[45]. In the practically important case of a random distribution of reactants and $N(0) \gg n(0)$ the solution has a simple form for the two limiting cases of $t \gg \tau_D$ and $t \ll \tau_D$ (where $\tau_D = a^2/D$ is the time for the diffusion of the reactants to a distance of the order of a). For $t \ll \tau_D$ (slow diffusion) the kinetics of the tunnelling reactions are described by Eqn. (26), and for $t \gg \tau_D$ (fast diffusion) by the equation

$$n(t)/n(0) = \exp\left[-\frac{4}{3}\pi R^3N(0) - 4\pi RDN(0)t\right], \tag{37}$$

where $R = \frac{1}{2}a\ln(\nu\tau_D)$ is the tunnelling distance in time τ_D.

As can be seen from Eqn. (37) the disappearance of the donors in this situation is described by the ordinary kinetic law for first-order reactions (the second term in the exponential). The two terms in the exponential of Eqn. (37) correspond to two possible mechanisms for the disappearance of reactants at time t. Thus, for a donor and an acceptor particle at a distance $r < R$ we have $[w(r)]^{-1} < \tau_D$, and electron transfer is the faster process, whereas for $r > R$ we have $[w(r)]^{-1} > \tau_D$, and the diffusional approach of the reactants is faster than the direct tunnelling mechanism. Hence donors and acceptors separated by a distance $r < R$ disappear by direct tunnelling transfer [described by the term $4/3\pi R^3N(0)$ in the kinetic equation (37)], and particles for which $r > R$ approach each other to a distance R and then react by the tunnelling mechanism [term $4\pi RDtN(0)$]. Thus the distance $R = \frac{1}{2}a \ln(\nu\tau_D)$ plays the role of a collision diameter in tunnelling reactions involving diffusion of the reactants.

We note from Eqn. (37) that, as predicted[57], the effective initial concentration of donors $n_{\text{eff}}(0) = n(0)\cdot\exp[-4/3\pi R^3N(0)]$, formally determined by extrapolating $\ln[n(t)]$ to $t = 0$, is lower than the real concentration by the number of donors which are initially within a sphere of radius R surrounding the acceptors, and which disappear by diffusionless direct tunnelling within a time τ_D from the beginning of the reaction. The activated nature of diffusion in condensed media is responsible for the monotonic increase of R with decrease of temperature.

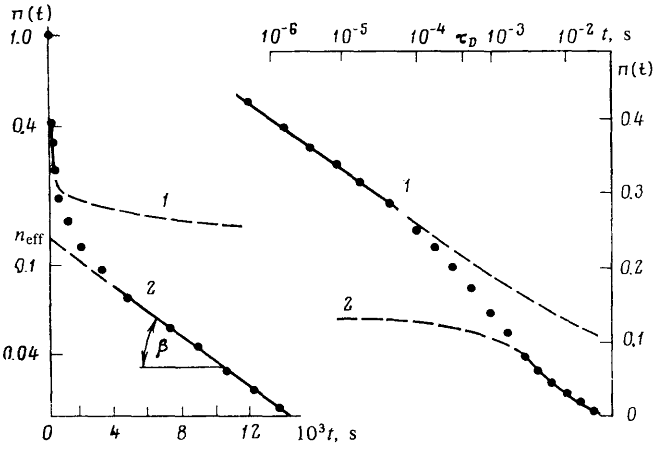

Figure 5. Kinetic curve for the reaction between e_{tr}^- and CrO_4^{2-} (2.5×10^{-2} *M*) in a 6 *M* aqueous solution of NaOH at 178 K. The points are experimental, the lines are theoretical curves calculated by Eqn. (26) (curve *1*) and Eqn. (37) (curve *2*) for $R = 31$ Å, $D = 2.2 \times 10^{-12}$ cm² s⁻¹ ($\tan\beta = 4\pi RDN$).

Miller[33] studied the kinetics of several reactions between e_{tr}^- and acceptors in an aqueous alkaline glass at relatively high temperatures under conditions such that $N(0) \gg n(0)$. By extending his measurements over a wide range of time (from 10^{-6} to 1 s) he was able to observe a change in kinetic law corresponding qualitatively to the transition from a tunnelling ($t \ll \tau_D$) to a diffusion mechanism ($t \gg \tau_D$).

We shall show that these results are described quantitatively by Eqns. (26) and (37). The experimental results[33] are compared in Fig. 5 with calculations by formulae (26) and (37). It can be seen that the initial portion of the kinetic curve is accurately described by formula (26) (curve *1*), whereas the final portion agrees with formula (37) (curve *2*). The numerical values of the diffusion coefficient ($D = 2.2 \times 10^{-12}$ cm² s⁻¹) and of the tunnelling distance ($R = 31$ Å) corresponding to curve *2* were obtained by linearising the final portion of the experimental kinetic curve in coordinates of $\ln[n(t)/n(0)]$ against t (Fig. 5). It can be seen from Fig. 5 that the value $\tau_D = a^2/D \simeq 4 \times 10^{-4}$ s corresponds to the transition from the kinetic regime described by Eqn. (26) to that described by Eqn. (37).

In principle the spatial distribution of reactants can alter not only as a result of thermal diffusion but also as a result of tunnelling diffusion through vacancies such as ionised donor particles or empty electron traps (in the case of e_{tr}^-). Kinetic equations for tunnelling reactions under conditions of tunnelling diffusion of electrons have been obtained by Khairutdinov[43], who showed that for short observation times $t \ll J^{-1}$ (where J is the probability of electron transfer by tunnelling diffusion from a donor to a vacancy in unit time), and when the concentration of acceptors in vacancies is much greater than the concentration of donors, the kinetics of the tunnelling reaction are described by Eqn. (26). In the opposite case ($t \gg J^{-1}$) the kinetics are described by an expression analogous to Eqn. (37) in which the quantity $D = \frac{1}{3}R^2/J^{-1}$ plays the role of a diffusion coefficient and R is the distance at which the probability of direct tunnelling recombination between the donor and the acceptor is comparable to the probability of a tunnelling diffusion jump.

An important consequence of that work[43] was the realisation that the kinetic equations for the direct tunnelling transfer of an electron from a donor to an acceptor and for the transfer of an electron by a series of tunnelling jumps into randomly distributed vacancies are quite different. This allows the two mechanisms to be distinguished. For example, the good agreement over a wide range of time between the experimental kinetic curves and those calculated by Eqn. (26) for the reaction of e_{tr}^- with $Cu(en)_2^{2+}$ suggests that this reaction involves direct electron tunnelling rather than the tunnelling diffusion of electrons along traps.

We have reviewed the kinetic equations for tunnelling reactions which can be used directly to analyse existing experimental data. Among the work which has not been discussed we should note a derivation[43] of the kinetic equations for tunnelling reactions under conditions of light-induced electron diffusion and an attempt[40,47,65] to allow for the effect of electrostatic interactions on the tunnelling recombination of charged particles in the presence of diffusion.

V. METHODS OF CALCULATING THE KINETIC CHARACTERISTICS OF TUNNELLING REACTIONS FROM EXPERIMENTAL DATA

The fundamental kinetic characteristics of tunnelling reaction are the parameters a and ν of Eqn. (12) for the probability of tunnelling in unit time. If a and ν are known we can calculate the probability $w(r)$ and the characteristic time $\tau(r) = w^{-1}$ for the tunnelling transfer of an electron to various distances, or the distance R_t to which the electron will tunnel in various times.

The parameters ν and a can be obtained from kinetic data on tunnelling reactions in solids only if the spatial distribution of the reactants is known. This requirement is met by reactions in glassy solutions under conditions such that one of the reactants (say, the acceptor A) was introduced before freezing the solution at a concentration much greater than that of the other reactant (the donor D). By preparing the samples in this way a random distribution of A particles in space can often be achieved[34,66]. It can be seen from Eqn. (26) that under these conditions the spatial distribution of the donors has no effect on the kinetics of the tunnelling reaction.

Kinetic curves are usually obtained by measuring the time dependence of the intensity $I(t)$ of lines in the optical or ESR spectra of the reactant present at lower concentration. The corresponding decrease in the intensity of the spectrum of the second reactant[29] or increase in the intensity of the spectrum of the reaction product[51] can also be monitored. From these measurements we obtain the ratio

$$n(t)/n(t_0) = I(t)/I(t_0),$$

where $n(t)$ is the time-dependent concentration of reactant, and $n(t_0)$ and $I(t_0)$ are the concentration of reactant and the spectral intensity at the beginning of the measurement. However the concentration term in Eqn. (26) is not $n(t_0)$ but $n(0)$, i.e. the concentration at time $t = 0$. Since the concentrations of reactants vary by an approximately logarithmic law in tunnelling reactions, $n(t_0)$ and $n(0)$ can be very different even for very short values of t_0. Direct measurement of $n(0)$ is impossible, and therefore $n(0)$ is usually replaced by the concentration n_c in control samples not containing the second reactant but otherwise identical in every respect with the experimental samples:

$$n(t)/n(0) = n(t)/n_c = I(t)/I_c; \tag{38}$$

where I_c is the spectral intensity of the control sample. The concentration of particles in the control sample is sometimes found to vary with time as a result of side reactions. In this case the ratio $n(t)/n(0)$ is replaced by $I(t)/I_c(t)$.[50,51]

In kinetic studies of tunnelling processes the reactant whose concentration is monitored is usually generated within the sample by radiolysis or photolysis so as to minimise the possibility of reaction during sample preparation. Under these conditions the assumption $n(0) = n_c$ is legitimate only if the tunnelling reaction between D and A is the only process by which the concentration of D can decrease in the presence of A. However in practice we cannot exclude *a priori* the possibility of a reaction of A with the precursors of D during radiolysis or photolysis. For example, the concentration of trapped electrons could decrease in the presence of acceptors not only as a result of the tunnelling reaction of e_{tr}^- itself, but also through the reaction of A with the precursors of e_{tr}^- (the so-called dry electrons[67]). As a result of such reactions the true initial concentration of donors $n(0)$ in the presence of A can be smaller than n_c (the concentration of D in the control samples not containing A). The quantities $n(0)$ and n_c are related by the expression

$$n(0) = n_c \exp[-\alpha N(0)]. \tag{39}$$

The parameter α characterises the efficiency with which the precursors of D are captured by the acceptor A. From Eqns. (26), (38), and (39) we obtain

$$I(t)/I_c = n(t)/n_c = \exp\left[-\alpha N - \frac{\pi a^3}{6} N \ln^3(\nu t)\right] \tag{40}$$

or

$$I(t)/I_c = n(t)/n_c = \exp\left(-\alpha N - \frac{4}{3}\pi R_t^3 N\right). \tag{41}$$

Thus if $N = N(0)$ is fixed the variation with time of $n(t)/n_c$ is determined by three independent parameters. These parameters can be evaluated by optimising the fit of Eqn. (40) to experimental data. The most obvious criterion of optimum fit is a minimum in the mean-square deviation of the experimental points from the theoretical curve plotted by using Eqn. (40).

Several methods of calculating the optimum values of ν, a, and α have been proposed[58]. In the simplest of these each parameter is varied in turn to give the best linearisation of the experimental kinetic curve in the coordinates which should give a linear plot according to Eqn. (40) or (41).

One of the methods of calculation depends on varying the parameter ν. Eqn. (40) can be written as

$$N^{-1} \ln [n_c/n(t)] = \alpha + (\pi a^3/6) \ln^3(\nu t). \tag{42}$$

It can be seen from this equation that after choosing the value of ν which gives the most linear kinetic plot of $N^{-1}\ln[n_c/n(t)]$ against $\ln^3(\nu t)$ we can find the best value of a from the slope, which is $\pi a^3/6$, and the best value of α from the intercept on the vertical axis.

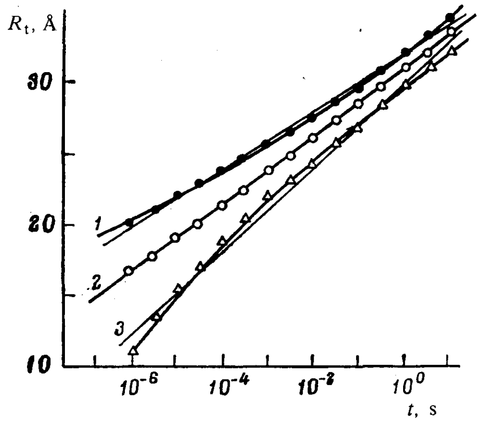

Figure 6. Kinetic plots of R_t against $\ln t$ for the reaction between e_{tr}^- and $K_3Fe(CN)_6$ (0.025 *M*) in 6 *M* aqueous NaOH at 77 K: *1*) $\alpha = 0$, *2*) $\alpha = \alpha_{opt} = 8.7$ M^{-1}, *3*) $\alpha = 2\alpha_{opt}$. Values of R_t calculated by formula (43) from the results of Ref. 33.

In another method of calculation the parameter α is varied. From Eqn. (41) we have

$$R_t = \{(3/4\pi N)[\ln(n_c/n(t)) - \alpha N]\}^{1/3}. \tag{43}$$

On the other hand, according to Eqn. (17), R_t should vary linearly with the logarithm of time. By choosing the best value of α we optimise the linearity of the experimental kinetic plot of R_t against $\ln t$. As before, the best value of a is obtained from the slope of the resulting straight line, which according to Eqn. (17) is $a/2$, and the best value of ν from the intercept on the vertical axis, which is $(a/2) \ln \nu$ (see Fig. 6).

A detailed analysis of these and other methods of calculating the parameters ν, a, and α can be found in Ref. 58, where it is shown that the results obtained by different methods are acceptably consistent (see, for example, Table 3). However, because of the logarithmic dependence of the concentration of reactants on time, the kinetic measurements must encompass a very wide range of observation times (not less than five orders of magnitude) for a reliable determination of the kinetic parameters of tunnelling reactions.

Table 3. Parameters ν and a calculated[58] by varying $\lg \nu$ (*1*) and α (*2*) from experimental curves for the decay of e^-_{tr} by reactions with different acceptors in aqueous-alkaline glasses at T = 77 K.

Acceptor	$\lg \nu$, [s^{-1}]		a, Å	
	1	*2*	*1*	*2*
BrO_3^-	11.0	11.2	1.30	1.29
$Co(NH_3)_6^{3+}$	10.9	12.1	2.24	2.05
$Fe(CN)_5NH_3^{2-}$	11.1	10.7	1.65	1.70
MoO_4^{2-}	12.5	11.8	1.41	1.48
$Fe(CN)_6^{3-}$	12.8	13.1	2.10	2.05
$Ni(CN)_4^{2-}$	13.9	13.9	1.31	1.31
IO_3^-	14.1	15.1	1.18	1.12
$Cr(CN)_6^{3-}$	14.9	16.0	2.02	1.92
ReO_4^{2-}	15.2	16.2	1.59	1.51
Np(VII)	15.5	12.9	2.29	2.65
Picrate	15.9	13.5	2.0	2.29
$Co(en)_3^{3+}$	15.7	15.8	1.91	1.90
$Co(CN)_6^{3-}$	17.9	18.4	1.39	1.35
NO_2^-	18.8	19.0	1.03	1.025
$ClAc^-$	20.3	19.6	0.35	0.36
Acrylamide	20.3	22 1	0.72	0.67
NO_3^-	18.6	18.4	0.98	1.02
$Cu(en)_2^{2+}$	15.5	15.0	1.79	1.87
CrO_4^{2-}	19.1	19.1	1.69	1.68

Eqn. (26) assumes that the parameters ν and a are the same for all pairs of reactants. The validity of this assumption has been demonstrated in Ref. 58 for tunnelling reactions in glassy matrices.

VI. KINETIC CHARACTERISTICS OF LONG-RANGE TUNNELLING ELECTRON TRANSFER REACTIONS

The most detailed studies of long-range tunnelling electron transfer are those devoted to the reactions of e^-_{tr} [18,20,29,31-35,57,68-76]. Currently known values of the parameters ν and a for reactions of e^-_{tr} are summarised in Table 3. These values were calculated[58] by analysing experimental data obtained[33,34,58] in kinetic studies of tunnelling reactions of e^-_{tr} extending over a sufficiently wide range of observation times (10^{-6}–10^2 s in Ref. 33 and 34, 10^{-6}–10^6 s in Ref. 58). As Table 3 shows, ν can vary over the very wide range from 10^{11} to 10^{21} s^{-1} depending on the nature of the acceptor, while a varies between 0.4 and 2.5 Å. The ranges of ν and a are very much greater than the experimental error in the determination of these parameters from the kinetic curves (not more than 15%).[58]

Table 4. Parameters ν and a for reactions of particles other than e^-_{tr}.

No.	Donor	Acceptor	Matrix	T, K	$\lg \nu$, [s^{-1}]	a, Å	Reference
1	NO_3^{2-}	CrO_4^{2-}	10 M $NaOH+H_2O$	77	20	0.9	77
2	$AgNO_3$	SO_4^-	6 M $H_2SO_4+H_2O$	77	6	1.3	49
3	$FeSO_4$	SO_4^-	ditto	4.2—77	7	1.8	48
4	$K_4Fe(CN)_6$	O^-	6.5 M $NaOH+H_2O$	4.2—77	12	1.8	48
5	$(C_6H_5)_2^-$	$C_{10}H_8$	ethanol + ether	77	7	1.7	50
6	$(C_6H_5)_2^-$	3-phenylethylene 0.01 M	ethanol	77	12.5*	1.98*	51
7	$(C_6H_5)_2^-$	3-phenylethylene 0.03 M	ethanol	77	13.8*	1.84*	51
8	$C_{10}H_8^*$	CCl_4	ethanol	77—140	—	—	53
9	Cd(I)	$Cr_2O_7^{2-}$	6 M $H_2SO_4+H_2O$	77	12	1.4	55
10	Cd(I)	MnO_4^-	6 M $H_2SO_4+H_2O$	4.2—77	14	1.3	55
11	Ni(I)	MnO_4^-	6 M $H_2SO_4+H_2O$	77	12	1.2	49

*Here $\lg \nu$ and a are the mean values of the parameters calculated[58] by varying $\lg \nu$ and α.

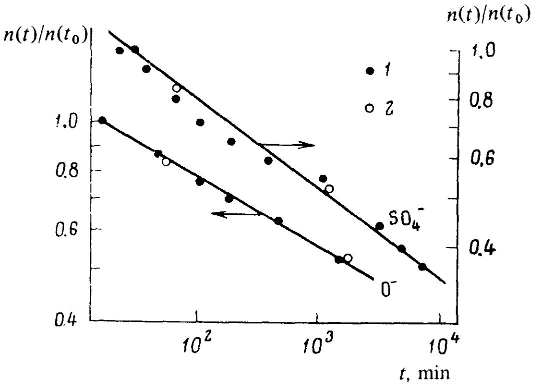

Figure 7. Kinetic plots of $n(t)/n(t_0)$ against $\lg t$ ($t_0 = 10^3$ s) for reactions (6) and (7a) at 77 K (points *1*) and 4.2 K (points *2*). The concentrations of $FeSO_4$ and $K_4[Fe(CN)_6]$ are 0.05 and 0.3 M respectively.

An outline of the reactions of particles other than e^-_{tr} is given in Table 4, which lists the kinetic characteristics of these reactions. For processes No. 6 and 7 the values of ν and a were obtained[58] by analysing kinetic curves extending over a wide (10^{-6}–10^2 s) range of time[51]. For the other reactions the kinetic curves were determined over a more limited range of time (not more than three orders of magnitude). As an example we show in Fig. 7 the kinetic curves for reactions (6) and (7a). From data of this type the parameters ν and a can be evaluated only if the parameter α is known from independent measurements[58]. Hence the ν and a values given in Table 4 were obtained by assuming α = 0 (except in the case of processes No. 6 and 7). These values, therefore, are an upper limit of the true value of ν and a lower limit of the true value of a.[58] As Table 4 shows, the range over which the parameters ν and a can vary in the different reactions is similar to the range of variation of these parameters for the reactions of e^-_{tr}.

We should note also that the values of ν and a (Tables 3 and 4) agree well with theoretical calculations[58] (see Chapter III).

Table 5. Temperature dependence of the parameters ν and a for the reactions between e_{tr}^- and various acceptors, calculated[58] from kinetic data[33] by varying lg ν (*1*) and α (*2*).

Acceptor	T, K	lg ν, [s^{-1}]		a, Å	
		1	*2*	*1*	*2*
$Co(en)_3^{3+}$	77	15.7	15.8	1.91	1.90
$Co(en)_3^{3+}$	143	11.1	13.1	2.5	2.2
CrO_4^{2-}	77	19.1	19.1	1.69	1.68
CrO_4^{2-}	147	10.0	10.9	2.97	2.74
NO_3^-	77	18.6	18.4	0.98	1.02
NO_3^-	143	10.6	10,6	1.69	1.49
BrO_3^-	77	11.0	11.2	1.30	1.29
BrO_3^-	143	13.0	11.5	1.02	1.13

The few data so far available on the temperature dependence of the parameters ν and a are summarised in Table 5. It can be seen that at least for the reactions of e_{tr}^- with CrO_4^{2-} and NO_3^- the parameter a increases very significantly with temperature. One possibility is that in these cases a new reaction path becomes available on raising the temperature, involving the excited electronic levels of the reaction products. In parallel with an increase of a we observe a decrease of ν, but overall the velocity of the reaction increases with temperature. On the other hand the variation of ν and a for the reaction of e_{tr}^- with BrO_3^- lies within experimental error, and for the reaction of e_{tr}^- with $Co(en)_3^{3+}$ is close to the limits of experimental error.

Conversely, the rate of the reaction of e_{tr}^- with biphenyl in 2-MTHF[78] and with benzyl chloride in C_2H_5OH [79] apparently increases as the temperature is lowered. As shown in the original papers, the influence of the acceptors on the radiation yield of e_{tr}^- decreases as the temperature increases from 4.2 to 77 K.

Thus the range of ν values in these tunnelling reactions extends from 10^6 to 10^{21} s^{-1}, and the range of a values extends from 0.4 to 2.5 Å. Both parameters depend on the nature of the electron donor and the electron acceptor, and they can decrease, increase, or stay constant when the temperature is increased. All these experimental findings are fully consistent with the theoretical model of long-range tunnelling electron transfer proposed in Ref. 58.

VII. CHEMICAL REACTIONS INVOLVING LONG-RANGE ELECTRON TRANSFER

Electron transfer reactions play an important rolè in various chemical situations. Many redox reactions in liquids or on solid surfaces, and also many electrochemical, radiation-chemical, photochemical, and biochemical changes include an electron transfer step.

The long-range electron transfer reaction allows chemical change to take place when the reactants are separated by a relatively large distance, thus offering interesting new possibilities in the organisation of chemical changes at the molecular level and in the control of these changes. These possibilities are fully utilised in the living world, for example in respiration and in photosynthesis[80]. The substances which take part in these complex biochemical processes are often immobilised in membranes, thus being prevented from undergoing undesirable side-reactions by collision processes. Nonetheless these substances can exchange electrons by a tunnelling mechanism[22,23,59,60,81-89]. The resulting oxidised and reduced forms can initiate chains of chemical reactions within their own region of the membrane.

We may assume that natural photosynthetic systems are able, by virtue of this type of organisation of chemical changes, to avoid fast recombination of the electrical charge pairs produced by the absorbed radiation, thus ensuring efficient photosynthesis. Separation of charges probably occurs by fast tunnelling electron transfer from the photo-excited chlorophyll (Chl) to the so-called primary acceptor (A):

$$\mathrm{Chl} \xrightarrow{h\nu} \mathrm{Chl}^* \xrightarrow{A} \mathrm{Chl}^+ + A^-.$$

The species Chl^+ and A^- initiate further chemical changes, leading ultimately to the evolution of oxygen from water and to the formation of carbohydrates from CO_2. The reverse electron transfer from A^- to Chl^+ is much slower. A possible explanation is the rapid conversion into heat of some of the energy stored in Chl^+ and A^- (the conditions which favour tunnelling electron transfer may be disturbed by lowering the energy levels); alternatively, the separation of the reactants may be increased by fast conformational changes in the membrane produced by the forward reaction. The fast recombination of light-separated charges is known to be the major obstacle to the design of artificial solar energy converters. By analogy with natural photosynthesis, the use of tunnelling processes would seem a promising way of overcoming these difficulties.

Table 6. Rate constants k_e for the reactions of e_{tr}^- with various acceptors in liquid solutions at 25° C and characteristic times τ for the reactions of e_{tr}^- with the same acceptors in solid aqueous-alkaline glasses at 77 K.

Acceptor	$10^{-10}k_e$, litre mole^{-1} s^{-1}	τ, s		
		R=10 Å	R=15 Å	R=20 Å
$ClAc^-$	0.12	$10^{4,6}$	10^{17}	—
NO_3^-	0.85	$10^{-9,9}$	$10^{-5,6}$	$10^{-1,3}$
$Cu(en)_2^{2+}$	1.8	10^{-10}	$10^{-7,5}$	10^{-5}

Tunnelling processes can be used to control the selectivity of redox reactions. This has not yet been achieved in practically important situations, however the possibility (in principle) of this type of control is shown by Table 6, in which we compare the rate constants for the reactions of hydrated electrons with three different acceptors in a liquid at 25° C and the characteristic times τ for the reactions of trapped electrons with the same acceptors in solid aqueous alkaline glasses at 77 K. It can be seen that in liquids, where the reactants can approach each other by diffusion (direct collisions), the rate constants for all three reactions are similar and very large. On the other hand in solids, where diffusion is negligible and the reactions take place by a tunnel mechanism, the characteristic times of the reactions vary with distance to different extents because of the differences in ν and a. For the reaction of e^-_{tr} with $Cu(en)_2^{2+}$ we obtain $\tau = 10^{-5}$ s even for $R = 20$ Å, and $\tau = 10^{-10}$ s for $R = 10$ Å. On the other hand the τ value for the reaction of e^-_{tr} with $ClAc^-$ is 14–15 orders of magnitude greater with $R = 10$ Å. This difference in the distance dependence of the time τ suggests the possibility of exploiting the tunnel effect for generating selectivity in redox reactions by creating barriers against direct collisions between the reactants. The gain in selectivity would be achieved at the cost of a loss in speed, but this could be unimportant in many fast electron transfer processes.

In solids there is practically no possibility of direct collisions between the reactants, and therefore the distance of the tunnelling transition (and hence the time τ) can be controlled by controlling the concentration of the reactants. In the case of liquids close approach between the reactants could be prevented by surrounding them with a shell of inert molecules (large ligands, or micelles). Experimental confirmation of the differences in tunnelling electron transfer behaviour between particles inside and outside a micelle has recently been obtained[90,91].

Long-range tunnelling electron transfer processes play an important role in radiation chemistry and in photochemistry. They enable many oxidation–reduction reactions in irradiated solid matrices to take place at rates well in excess of the diffusion-limited rate.[57] The tunnelling recombination of positive and negative ions can set a limit to the steady-state concentration of these particles in radiolysis[21], and it can produce time-changes in the radiation-chemical yield[57].

Long-range electron transfer can be important also in the protection of materials from radiation damage and photo-degradation[92,57]. By using the tunnel mechanism the photochemical changes of some organic materials in solids can be made to occur by a one-photon rather than a two-photon process, i.e. with a smaller energy input[52].

Tunnelling electron transfer is very relevant also in oxidation–reduction catalysis, including enzyme reactions. Thus it has been shown[93] that the two-electron reduction of molecular oxygen to hydrogen peroxide by Cu^+ ions immobilised in blue (copper-containing) oxidases is thermodynamically unfavourable. Hence we may assume that molecular oxygen is reduced directly to water when complexed with the active centres of these enzymes[94]:

$$4Cu^+ + O_2 + 4H^+ \rightarrow 4Cu^{2+} + 2H_2O.$$

It appears that two electrons are transferred from copper ions directly bound to oxygen in the complex, and two additional electrons are transferred from more remote copper ions in the enzyme molecule.

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Radical Pairs in the Study of Elementary Chemical Reactions in Solid Organic Substances

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Methods for the investigation of elementary chemical reactions and molecular motions on the basis of the EPR spectra of radical pairs are examined. The results of the study of the stereochemistry and kinetics of processes involving radical pairs are used to discuss the nature of the characteristic features of the elementary solid-phase reactions: the existence of a broad spectrum of the frequencies of the reactions and molecular motions, the reaction mechanisms at low temperatures, and the influence of intra- and inter-molecular motions on the rates of chemical reactions.

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I. INTRODUCTION

Studies on elementary chemical processes in solid organic substances, which were initiated to a large extent in the research of Academician V.V.Voevodskii[1], are developing vigorously at the present time. These studies are fundamentally closely related to fields of modern science such as the physical chemistry of polymers, molecular biology, and radiation chemistry. In contrast to elementary gas-phase reactions, where energy transfer, excitation, and excited state relaxation processes are most significant (and responsible for the rate of the chemical reaction), in the solid state an analogous role is apparently played by phenomena of a quite different type: translational and rotational motions, conformational rearrangements of molecules, etc.

In the study of reactive species in condensed media spectroscopic and microwave spectroscopic methods are of greatest importance. However, it is difficult to use even these methods to investigate elementary processes of the above type, because rotation and conformational transitions usually have only a weak influence and translational displacements have no influence at all on the spectra of individual species. The aim of the present review is to show that, in relation to radical reactions which play an important role in the chemistry of solid organic substances, considerable progress may be achieved by investigating radical pairs, i.e. radicals separated by a "molecular" distance (3–10 Å). Such radical pairs are, as it were, "entropically excited" intermediates in dissociation-recombination and disproportionation reactions. The high sensitivity of the EPR spectra of radical pairs to a relative displacement of the reaction centres has proved to be most significant, and makes it possible to obtain in many instances detailed information about the elementary processes in solids.

It has been shown a comparatively long time ago that, when stable radicals adjoin one another, the interaction between unpaired electrons greatly alters the spectrum. This permits the determination of the distance between the electrons[2]. There was a growth of interest in the "chemical" applications of this phenomenon after the discovery of the possibility of detecting metastable radical pairs, consisting of active radicals formed as a result of the decomposition of molecules in the solid phase[3]. Since 1966–1967, studies in this field have led to the detection and investigation of radical pairs in many chemical systems; these investigations have been surveyed in monographs[4,5] and reviews[6,7]. However, the above reviews were devoted mainly to problems of the formation of radical pairs and the analysis of their EPR spectra. As far as we are aware, the present review is the first attempt to survey new data on the kinetics of elementary physical and chemical processes obtained in the study of radical pairs. We hope that this survey will make it possible to formulate more clearly the possibilities arising as a result of the development of this field of research.

II. METHODS FOR THE INVESTIGATION OF RADICAL PAIRS

The theory of the EPR spectra of radical pairs has been described in detail in reviews[8,9] and monographs[10,11]. Here we shall consider the main theoretical conclusions directly applicable to the study of elementary reactions in the condensed phase.

1. EPR Spectra of Radical Pairs

A pair of radicals separated by distance $r \leqslant 10$ Å constitutes a system with two interacting electrons having an overall spin $S = 1$ and hence a multiplicity $2S + 1 = 3$. The dipole–dipole interaction between the electrons removes the degeneracy of the levels in the "zero field". The energy of the states and the transitions in the case of axial symmetry, where the energies of the T_1 and T_{-1} states in the zero field are the same, are illustrated in Fig. 1. When the magnetic field H_0 is scanned using a fixed frequency, it is possible to observe two allowed $\Delta M_S = 1$ transitions corresponding to the reversal of a single spin in the magnetic field. The splitting in this instance is

$$D = \frac{\xi g\beta}{r_{\text{cp}}^3}(3\cos^2\alpha - 1) \quad , \tag{1}$$

where r_{av} is the length of the appropriately averaged vector connecting the unpaired electrons of the free radicals, α the angle between the interelectron vector $\vec{r}_{av}$ and the direction of the permanent magnetic field H_0, g the spectroscopic splitting factor, assumed to be isotropic, β the Bohr magneton, and ξ a numerical coefficient equal to 3/4 for resonance spins (having the same Larmor precession frequency) and 1/2 for non-resonance spins.

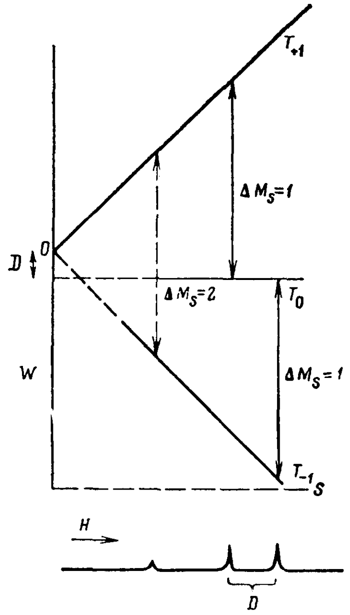


Figure 1. Energies of the states and transitions responsible for the EPR spectrum of the radical pair in a single crystal.

In the absence of axial symmetry, the degeneracy is fully removed in the zero field. The energies are then usually formulated in terms of two independent parameters D and E:

$$T_1 = 1/3D - E + g\beta H_0,$$
$$T_{-1} = 1/3D + E - g\beta H_0,$$
$$T_0 = -2/3D.$$

For radical pairs, $E \ll \frac{1}{3}D$ in most cases, and the difference between T_1 and T_{-1} in the zero field may be neglected without a significant loss of accuracy[12].

2. Determination of Spectroscopic Parameters

Determination of the fine structure parameters. The quantity $D_{\parallel}$ (i.e. D corresponding to $\alpha = 0$), the average distance between the unpaired electrons r_{av}, and the orientation of the interelectron vector of the radical pair relative to the crystallographic axes can be determined from the dependence of the fine splitting in the pair D on the orientation of the single crystals in the magnetic field.

The quantity $D_{\parallel}$ may be measured also on the basis of the EPR spectra of randomly oriented systems, which can be established experimentally in polycrystalline and vitrified specimens. The calculated line form for axial symmetry and on the assumption of a small line width is presented in Fig. 2. In the case of large line width and poorly resolved EPR spectra the rules obtained with the aid of model calculations of the line form[13] must be used in the determination of $D_{\parallel}$. When there is a significant deviation from axial symmetry, the intense "perpendicular" peaks illustrated in Fig. 2 are split by an amount $3|E|$. This usually makes it possible to determine both spectroscopic parameters (D and E). The same parameters can be found when the single crystal is rotated about two perpendicular axes after finding the principal values and directional cosines of the experimental splittings tensor in a zero field[10]. The $\Delta M_S = 1$ transition is frequently not observed in radical pairs owing to the considerable extent of the spectrum, the broadening of the lines caused by the scatter of the distances r_{av}, or very frequently, owing to the superposition of the intense signal due to isolated radicals. In this case one investigates the weak signal of the "forbidden" $\Delta M_S = 2$ transitions (Fig. 1), formally corresponding to the simultaneous reversal of two spins. The finite probability of the "forbidden" transition is due to the mixing of the T_0 and T_{+1} levels as a result of the dipole–dipole interactions; for the usual formulation of the experiment (EPR in perpendicular fields), it is given by[8]

$$\varphi = 2\frac{D_{\parallel}^2}{H_0^2}\sin^2 2\alpha = 2\left(\frac{3g\beta}{2r_{cp}^3 H_0}\right)^2 \sin^2 2\alpha; \tag{2}$$

when $D_{\parallel} \simeq 10^2$ G and $H_0 = 3 \times 10^3$ G, we have $\varphi \lesssim 10^{-3}$.

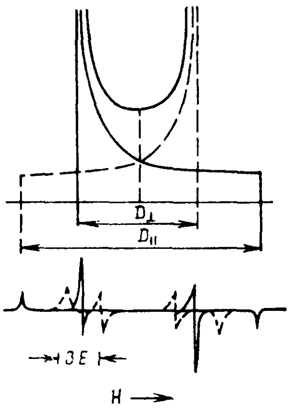


Figure 2. Theoretical EPR spectrum of polyoriented radical pairs (absorption corresponding to infinitesimal line width and the derivative of the absorption curve obtained taking into account the finite line width) for an axially-symmetrical tensor D. The additional splitting of the lines in the absence of axial symmetry ($D_{\parallel} = 2D_{\perp}$) is shown below by dashed lines.

However, the observation of "forbidden" transitions becomes possible when the line width is smaller and a higher microwave power is used[14]. The position of the centre of the $\Delta M_S = 2$ transition is determined by the condition

$$H^2 = 1/4H_0^2 - 1/3\,(D^2 - 3E^2),$$

i.e., when $D \ll H_0$, the position of the line virtually coincides with $H_0/2$; the shift $\delta H \simeq D^2/6H_0$ of the line may be used to determine D, but it is usually impossible to measure it.

Another method for the determination of D, proposed by Grinberg et al.[15], is based on the measurement of the shift of the saturation curves, i.e. the dependence of the signal intensity I on the amplitude of the microwave field H_1. If the spin–lattice relaxation times of the radicals and radical pairs are the same, then the I–lg H_1 saturation curves are displaced by an amount $\Delta = \lg \varphi$ (for a single-crystal), which makes it possible to determine φ and D. For polyoriented specimens, the analysis is more complicated but the simultaneous measurement of the shift Δ of the relative signal intensity $I_{\Delta M_S=2}/I_{\Delta M_S=1}$ frequently permits the determination of φ and D.[15]

Determination of the hyperfine structure parameters. The hyperfine interaction in the radical pairs leads to additional splitting of the levels of the triplet state ($S = 1$; $M_S = 1, 0, -1$):

$$T_1 = g\beta H_0 + 1/3D + \sum A_i M_{Ii},$$

$$T_{-1} = -g\beta H_0 + 1/3D - \sum A_i M_{Ii},$$

$$T_0 = -2/3D,$$

where the summation is carried out over all the interacting nuclei of the radical pair. Although the electronic spin moment in the triplet state is the moment of two bound electrons ($S = 1$), on average only half of this moment interacts effectively with the nuclei of each individual radical. Two electrons cannot be present in the same orbital and for this reason they occupy different normalised molecular orbitals,

$$\psi_1 = 1/\sqrt{2}\{\psi(R_1) + \psi(R_2)\},$$

$$\psi_2 = 1/\sqrt{2}\{\psi(R_1) - \psi(R_2)\},$$

formed by the combination of the orbitals of the unpaired electrons of the isolated radicals R_1 and R_2. Consequently the resulting spin density for each radical in the pair is the same as for the isolated radicals. Since the distance between the radicals is large, the magnetic cross-interaction of the nuclei of R_1 with the electrons in R_2 is negligibly small. Ultimately the splitting of the $M_S = \pm 1$ energy levels is the same as for $M_S = \pm 1/2$. For the allowed $\Delta M_S = 1$ transition, the hyperfine interaction constants for the radical pairs are equal to half the hyperfine interaction constants for the isolated radicals (Fig. 3). The same situation obtains for $\Delta M_S = 2$ transitions when the hyperfine interaction constants are expressed in magnetic field units[8].

It is noteworthy that the hyperfine interaction constants measured in "perpendicular" or "parallel" components of the spectrum of the radical pairs (Fig. 3) may refer to quite different orientations of the hyperfine interaction tensor in the magnetic field. This makes it possible to determine the orientation of the radical fragments relative to the axis of the pair.

Extent of the exchange interaction. In considering the EPR spectra we have hitherto assumed that the system is in the triplet state. In reality the triplet state of radical pairs is usually separated from the nearest singlet state by an energy gap which is very small compared with kT. All four levels are equally populated, so that 1/4 of the radical pairs do not give rise to an EPR signal. Yet another interesting case arises when the singlet–triplet splitting $E_T - E_S = J$ is greater than kT but is nevertheless fairly small and the triplet becomes thermally attainable without a significant mixing of the states. In this case it is possible to determine the exchange integral from the temperature dependence of the EPR signal intensity of the triplet state, because the signal intensity $I_{\Delta M_S=1} \simeq 3T^{-1}\exp(-J/kT)$. The latter

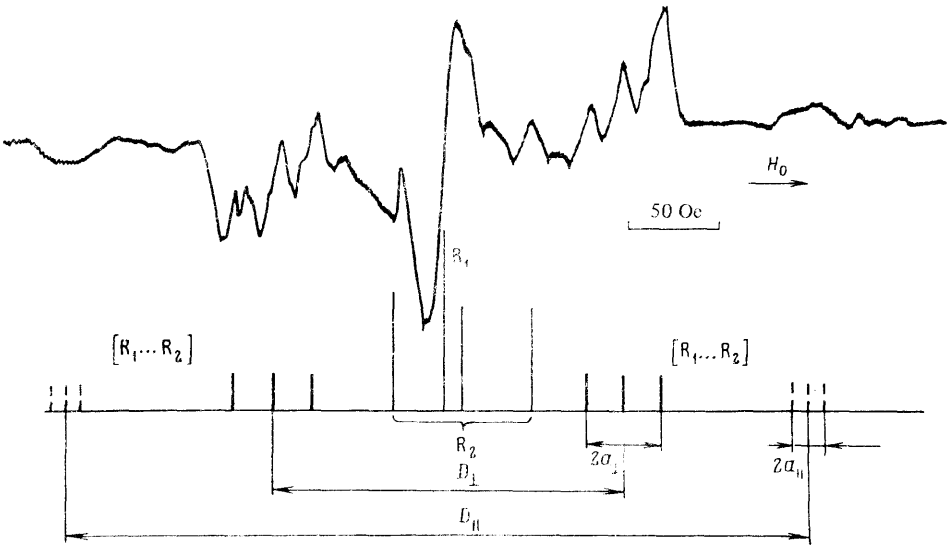


Figure 3. The real EPR spectrum of the "iminoxy–phenoxy"-radical pair and the isolated radicals in γ-irradiated polycrystalline o-nitrophenol and the conditions used in the interpretation of the spectrum. Evidently the hyperfine splitting in the spectrum of the radical pair is smaller by a factor of two than in the spectrum of the isolated radicals and is different for parallel and perpendicular orientations.

is of particular interest for chemistry, since the dependence of J on r_{av} determines the magnetic effects in chemical reactions[16]. The quantity J has been determined[17,18] for different values of r_{av} in radical pairs. Effects arising from the distortion of the hyperfine structure, caused by the mixing of the T_{+1} (or T_{-1}) and S_0 levels, have been used for this purpose[19,20] and not the temperature dependence of the EPR signal intensity.

3. Determination of Structural Parameters

In those cases where the point dipole approximation is valid, the dipole–dipole interaction leads to fine splitting of D in the spectrum of the radical pair described by formula (1). This formula may be replaced by an equivalent expression which is convenient for the interpretation of experimental data:

$$D=\frac{1}{2}D_{\parallel}(3\cos^2\theta\cdot\sin^2\psi-1), \quad (3)$$

where θ is the angle between the projection of the interelectron vector and the direction of the magnetic field H_0, ψ the angle between the interelectron vector and the axis of rotation of the crystal, and $D_{\parallel}=55\,600/r_{av}^3$ (for resonance spins); D and $D_{\parallel}$ are expressed in gauss and r_{av} is expressed in angstroms. The crystallographic axes are selected as the axes of rotation of the single crystals. Fig. 4 presents the experimental[21] relations between D and the angle θ for pairs of iminoxy-radicals. In order to determine the positions of the detected radical pairs in the unit cell of the dimethylglyoxime crystal, parameters characterising the structures of all possible pairs of iminoxy-radicals with $r_{av} \leq 6$ Å were calculated. It was assumed[8] that the spin density is localised at the NO bond, that the electron densities at the atoms are $\rho_O = 0.67$ and $\rho_N = 0.33$, and that the same spin density distribution is maintained approximately in all the radical pairs.

The theoretical relations are compared in Fig. 4 with the experimental relations; their agreement shows quite clearly that irradiation results in the formation of all the possible types of pairs and that the distances between them are close to those in the undisrupted crystal lattice. In determining the orientations of pairs of radicals with delocalised electrons, account must be taken of the degree of delocalisation. Thus allowance for delocalisation in a pair of diphenylnitrogen radicals in tetraphenylhydrazine[18] gave values of r_{av} differing by ~1 Å from those calculated in terms of the point dipole approximation. However, in these calculations no account was taken of the form of the orbitals of the unpaired electrons. A calculation of r_{av} with allowance for the form of the orbitals has been carried out[22], which made it possible to determine the structure of the complex from which radical pairs are formed as a result of subsequent phototransfer of a proton.

4. Measurement of the Concentration of Radical Pairs

Since radical pairs have an effective spin $S = 1$ and stable radicals with $S = 1/2$ are used as the standards in EPR, account must be taken of the difference between the transition probabilities for systems with different spins. The EPR signal intensity (I) in the absence of saturation is proportional to the number of species N and to the square of the magnetic moment $\mu^2 = g^2\beta^2S(S+1)$, i.e.

$$I \propto NS(S+1).$$

If the specimen contains N radical pairs, then only 3/4 of them populate the magnetic (triplet) levels T_0 and $T_{\pm1}$ (Fig. 1), and for this reason we have $I \simeq \frac{3}{2}N$ when $S = 1$. For N_R isolated radicals with $S = 1/2$, the intensity $I \simeq \frac{3}{4}N_R$. Thus, in the standard determination of concentration from EPR spectra, one obtains twice the number of radical pairs, i.e. the number of radicals combined into pairs. If no account is taken of this, one can make an error by a factor of two in the calculation of the concentration.

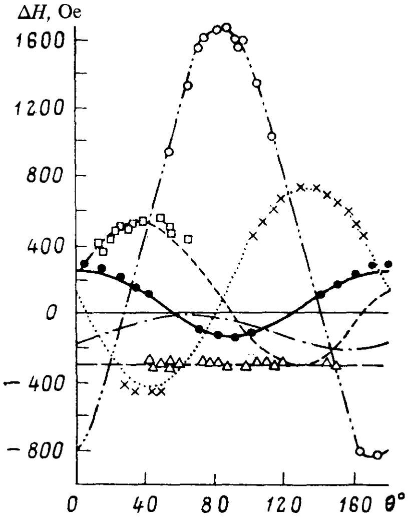


Figure 4. Experimental (circles) and theoretical (lines) angular relations for the hyperfine splitting constant D corresponding to the rotation of a dimethylglyoxime single crystal about the crystallographic a axis for five types of pairs with $r_{av} \leqslant 6$ Å. Comparison of the experimental points and the calculated curves makes it possible to identify the positions of the radical pairs in the unit cell of the crystal[21].

When account is taken of the differences between the transition probabilities described, the determination of concentrations from EPR spectra does not differ from the usual procedure, i.e. one compares the areas of the EPR signals of the test and reference specimens. The following useful relation has been obtained for the estimation of the area under the absorption line (s), recorded as a derivative line[23]:

$$s = kI'_{\perp}(3/2D_{\perp})^{1/2}\delta_{\perp}^{3/2},$$

where $I'_{\perp}$ and $\delta_{\perp}$ are the intensity and the apparent width of the "perpendicular" component (Fig. 5), while the shape coefficient $k \simeq 1/2$ for a Gaussian form of the individual line and $k \simeq 2$ for a Lorentzian form. A relation of the same type (but with different coefficients) makes it possible to express the area in terms of the intensity of the "parallel" component. A more accurate but cumbersome method of determining the area under the EPR signal consists in double integration or evaluation of the first moment of the experimental line.

If the usual $\Delta M_S = 1$ transition is not observed and only "forbidden" $\Delta M_S = 2$ signals are recorded, the problem of the determination of the concentration of radical pairs becomes significantly more difficult, because absolute calculations require the knowledge of the transition probability φ defined by Eqn. (2). A method has been proposed[15] for measurements based on the shift of saturation curves. In fact, for polyoriented radical pairs it is also necessary to average $\varphi(r, \alpha)$ with respect to orientations; nevertheless joint measurement of the $\Delta M_S = 2$ signal intensity and of the shift of its saturation curve relative to the signal of the radicals makes it possible to determine the concentration of radical pairs and the distance between the unpaired electrons[15].

In conclusion of the methodological part of the review, one must emphasise that the simultaneous determination of the hyperfine interaction constants and the fine structure constants, of the distance between the radicals (to within 0.1 Å), and of the orientation of the pair makes it possible to determine almost ambiguously the structure of the active centre and its position in the matrix. By studying the variation of these parameters during the course of a reaction, we have a unique possibility of investigating the "stereometry" of an elementary chemical process in a solid matrix.

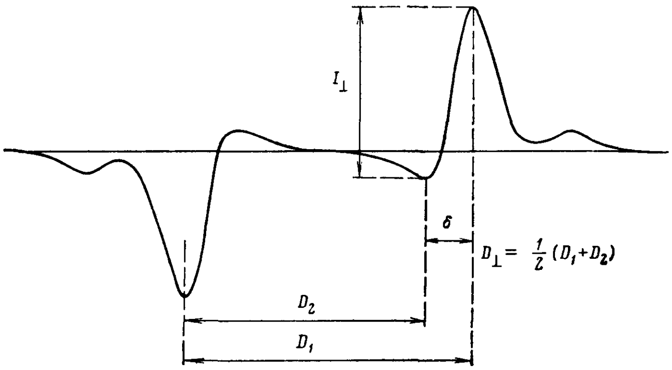


Figure 5. EPR spectrum of randomly oriented radical pairs with a large width of the individual lines and the parameters used to analyse the poorly resolved spectra[13,23].

III. THE PRIMARY STAGES IN RADIOLYSIS AND PHOTOLYSIS

In conformity with the principle of the conservation of valence, any process involving the formation of radicals from neutral molecules should proceed via a radical pair formation stage. Direct detection of radical pairs should naturally yield valuable information about the mechanisms of the reactions leading to the formation of the active centres—free radicals in solid matrices. In particular, the structure of metastable radical pairs, their orientation, and other characteristics may be used to elucidate the mechanisms of the reactions in solids under the influence of light and ionising radiation.

1. Photodissociation in the Solid Phase. Primary Steps of Photolysis

As already mentioned, in the photolysis of many solid organic compounds it is possible to detect metastable radical pairs[3,18,24]. Interesting data on the mechanism of the primary steps of photolysis have been obtained by magnetophotoselection of radical pairs. The effect of the steric selection of triplet molecules under the influence of polarised visible light is comparatively little known[25]. The magnetophotoselection effect of this kind was observed for the first time[26-28] in the formation of radical pairs under the influence of linearly polarised ultraviolet light.

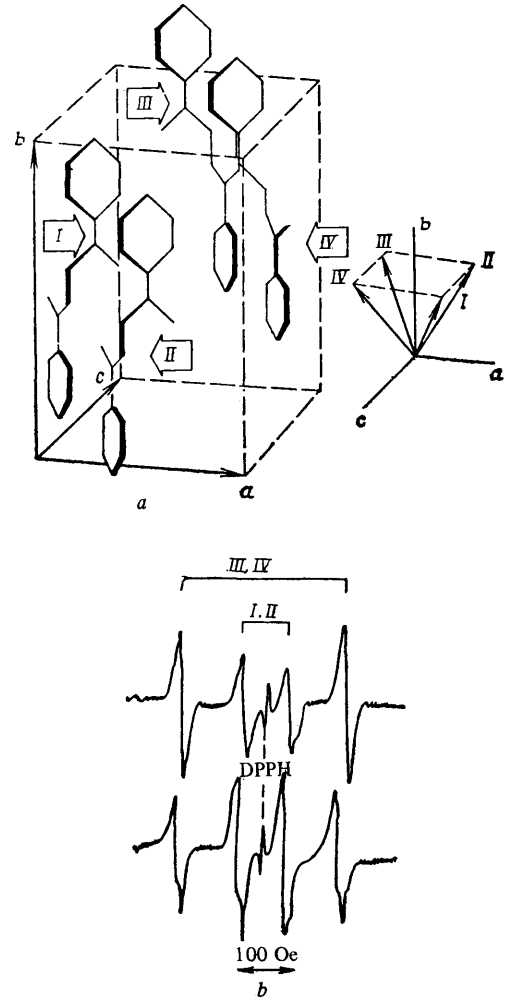


Figure 6. *a*) Schematic illustration of the orientation of different types of radical pairs in the unit cell of a benzoyl peroxide crystal; the arrows indicate the positions of the CO_2 groups evolved on photolysis[28]; *b*) selective accumulation of the EPR signals of radical pairs on photolysis with linearly polarised light: above—electric field strength $e \parallel (1,\bar{1},0)$; below—$e \parallel (1,1,0)$. The spectra were recorded for the $H_0 \parallel (1,\bar{1},0)$ orientation.

The formation of radical pairs in acridine–acridan single crystals under the influence of linearly polarised light has been studied by EPR.[27] The directions of the dipole moments of the transitions were found from the dependence of the quantum yield of radical pairs on the angle between the electric field strength vector **e** and the crystallographic axis. In the range 250–400 nm the dipole moment of the transition is in the plane of the acridine molecule and is directed along the *c* axis; in the range 380–540 nm the component of the dipole moment of the transition is perpendicular to the plane of the molecule and is directed along the *b* axis. These results are consistent with data showing the anisotropy of the absorption of polarised light by the acridine molecule[29] and illustrate the advantages of the EPR study of the anisotropy of the absorption of light in single crystal specimens.

For benzoyl peroxide[28], the transition in the range 300–330 nm corresponds to electron transfer along the C–O bond (O is the oxygen of the peroxide bridge). The existence of four radical pairs with non-equivalent orientations in the benzoyl peroxide single crystal (Fig. 6) and the distance between the radicals, which is 5.4 Å, indicate the formation of the $PhCO_2^{\bullet}$ and $Ph^{\bullet}$ radicals on photolysis. One of the two symmetrical CO_2 groups, oriented in different ways in the cell, can be selectively abstracted by polarised light, i.e. the primary excitation is localised at one of the two symmetrical benzoxy fragments. This permitted the conclusion that there is no rapid transfer of excitation between the two equivalent fragments of the benzoyl peroxide molecule.

The analysis of the EPR spectra of polyoriented systems is more complex; nevertheless, by studying the angular distribution of the primary photolysis products (radical pairs), it is possible to determine the direction of the transition moment and the nature of the photodissociation step. Thus, for the dissociation of tetraphenylhydrazine,[26] the best agreement between the theoretically calculated EPR spectra of partly oriented radical pairs and experimental spectra was observed when the transition moment coincided with the direction of the N–N bond in the molecule and for an angle of 62° ± 3°C. It has been found analogously[30] that the vector of the electronic transition moment, excited by polarised light in 3,6-di-t-butyl-*o*-benzoquinone, is at an angle of 70° ± 5°C relative to the plane of the molecule. In both cases the polarisation of the transition corresponds to the electron transfer from the heteroatom to the benzene ring (an $l-\pi^*$ transition) and the observed directions of the vectors agree with the ideas concerning the geometry of the wave functions in complex organic molecules.

The whole of the information about the structure of the radical pair and about the nature of the excitation step suggests also a mechanism for the photoinitiation of radical pairs. Thus it has been shown[27,30] that selectively excited molecules in the singlet state abstract hydrogen atoms from neighbouring molecules, forming radical pairs.

2. The Mechanism of the Radiolytic Generation of Radical Pairs

The mechanism of radiolysis is of special interest for the chemistry of elementary radical reactions, because it determines the initial steric distribution of radicals.

A large series of studies on radical pairs[12,31-36] made it possible to approach from new standpoints an understanding of the mechanism of the formation of radicals in radiolysis. However, there is no final view concerning these problems. The situation is similar as regards the question of whether the same mechanism operates in the formation of isolated radicals and radicals stabilised in a matrix in pairs and separated by short distances. Radical pairs may be formed in different ways[12,31,32]:

$$\begin{array}{rl}
\text{I.} & R_1{-}R_2 \rightsquigarrow [R_1R_2]\ ,\\
\text{II.} & [RH \ldots RH] \rightsquigarrow [RH^+RH^-] \to [R \ldots RH_2]\ ,\\
\text{III.} & [RHRH] \rightsquigarrow [RH \ldots RH]^* \to [R \ldots R] + H_2\ ,\\
\text{IV}\,a. & RH \rightsquigarrow RH^+ + e^-\ ,
\end{array}$$

$$\begin{array}{rl} b. & RH^+ + e^- \to \\ c. & RH + H \to \end{array}\left[\begin{array}{c} R \\ R \end{array}\right]\begin{array}{l} + H\ ,\\ + H_2\ ,\end{array}$$

$$\text{V}\,a.\ RH \rightsquigarrow RH^+ + e^-\ ,$$

$$\begin{array}{rl} b. & RH^+ + RH \to \\ c. & RH_2^+ + e^- \to \end{array}\left[\begin{array}{c} R \\ R \end{array}\right]\begin{array}{l} + RH_2^+\ ,\\ + H_2\ .\end{array}$$

According to a number of data[24,31,32,37-43], it is seen that radical pairs at concentrations comparable to or greater than those of isolated radicals are generated in compounds capable of forming complexes in solutions and containing functional groups giving rise to hydrogen bonds. A probable mechanism of the formation of radical pairs may be pathway II–III, where the complex decomposes with charge transfer or excitation of the complex. A characteristic feature of this pathway is the stereospecificity in the formation of pairs, since a complex may be formed only from molecules oriented in a particular manner relative to one another in the solid phase.

The formation of radical pairs at concentrations lower by 1–2 orders of magnitude than those of isolated radicals takes place in the radiolysis of paraffins, polyolefins, and other polymers which do not contain active functional groups (for example in polyethylene[32], acrylic polymers[44], n-eicosane[45], vinyl monomers[46], etc.). This results in the formation of several types of pairs[12,35,47]. In the given instance one should consider only mechanisms IV and V, because the relaxation of molecular excitation in the condensed phase is very effective and ion-molecule processes play the main role. It has been shown[32] that the introduction of bromodecane into n-decane lowers the yield of radical pairs. The replacement of hydrogen in n-decane by deuterium has a similar influence[34]. This points directly to mechanism V. Reaction Vc may not in fact lead to the formation of an alkyl radical. If it entails the formation of RH and H, the isolated radical is stabilised by reaction IVc.

Many new characteristics of the mechanism of the formation of radical pairs have been observed in the latest studies of the low-temperature radiolysis of olefins and polymers[12,35]. It has been found that, when the radiolysis takes place at lower temperatures (1.5–4 K), then the yield of pairs exceeds that of isolated radicals and virtually all types of radical pairs which can be formed in the crystal cell are in fact formed at concentrations proportional to their statistical weight. The random formation of pairs is in poor agreement with mechanism V, where the third stage is undoubtedly stereospecific and sensitive to the distance over which H^+ or D^+ is transferred. The increase in the yield of radical pairs following the replacement of H and D and with increased length of straight-chain hydrocarbons, functioning as boundary lines limiting the free migration of H or D, also supports mechanism IV. However, the mechanism of the temperature dependence of the migration of H and D following irradiation remains incomprehensible. Similarly, it has been deduced[12,36] that there is a specific mechanism of the formation of compact pairs on the basis of the observation that the yield of pairs with a small distance between the radicals exceeds the random yield.

It has been shown[36] that irradiation with large doses at 77 K is characterised by yet another interesting feature. Despite the high overall concentration of radicals, randomly formed radical pairs are absent from the system. The concentration of pairs increases synchronously with increase of the concentration of radicals, while the formation of radical pairs should have led to the observation of a quadratic relation at higher concentrations. A "protective" mechanism begins to operate, preventing the formation of new radicals within a sphere having a radius of 10 Å around a radical which has been stabilised. In frozen solutions of stable radicals at the same concentration randomly formed pairs are stabilised at concentrations corresponding to normal statistics.

3. Steric Distribution of Radicals on Radiolysis

Data for the formation of radical pairs on radiolysis can be used to determine the complete picture of the steric distribution of radicals in irradiated solids. Studies of the role of track effects in the steric distribution of radicals, carried out by the electron spin echo method[47,48], have shown that on γ-radiolysis the overlapping of tracks begins for very low doses (~0.1 Mrad). Consequently, for the usually employed doses of 1-100 Mrad, the role of track effects may be neglected and the distribution of species throughout the specimen may be regarded as uniform. On the other hand, the data presented in the previous section demonstrated the appreciable role of pair stabilisation in the steric distribution of active centres. Furthermore, it has been shown[12,35] that, when the radiolysis is carried out at 1.5 and 4.2 K, 91% of the radicals in $C_{10}D_{10}$ are stabilised in pairs. All possible types of pairs are formed with equal probabilities from 26 nearest adjoining molecules, i.e. the distribution with respect to distances is virtually rectangular:

$$\frac{dc}{dr}=\begin{cases}0 \text{ when } r<2.5\text{Å} \text{ and } r>30\text{Å}\\ \dfrac{c}{r_{\max}-r_{\min}} \text{ when } 2.5\text{Å}<r<30\text{Å}\end{cases}, \tag{4}$$

where $r_{\min}$ and $r_{\max}$ determine the set of possible distances r_{av} between arbitrarily selected nearest C-H bonds. In other words, there is a random distribution in pairs. The form and width of their distribution depends on the irradiation temperature and on the isotopic concentration of the substance: with increase of temperature and following the replacement of $C_{10}D_{10}$ by $C_{10}H_{10}$, the width increases. Furthermore, in all cases the formation of pairs is accompanied by destruction and valence migration reactions[12,35] which necessitate a correction to the initial distribution. The distribution widens in the direction of higher values of r_{av} and there is partial "annealing" of pairs with small values of r_{av}. It is of interest that in polyethylene and in $C_{10}H_{10}$ the form of the distribution is independent of the dose up to 330 Mrad. The situation is different in the γ-radiolysis of dimethylglyoxime,[49] where the distribution of isolated radicals changes with increasing dose, which is manifested by an increase in the order of the recombination reaction from first to second. Thus, on low-temperature radiolysis, the radicals are initially distributed at random in pairs.

4. Conditions Governing the Stabilisation of Radical Pairs in the Matrix

The formation of radical pairs involves primarily the generation of non-equilibrium defects. Their relative stability is determined by the partial rearrangement of the molecule and the matrix. The recombination of radicals in the pair is activated even in those cases where the radical centres are nearest neighbours. The rearrangement of the matrix, stabilising the radical pairs, should seemingly cause a scatter of the parameters of the radical pairs (the distance r_{av} and orientation). However, the EPR spectra of radical pairs described in the literature indicate a surprising constancy of the distance between the radicals. For the $\mathrm{Ph^{\bullet}...CH_3^{\bullet}}$ pair, it is possible to record a hyperfine splitting of the β-protons of the phenyl radical with a constant of 3 G.[24] This implies that the scatter of the parameters should be less than 3 G, i.e. less than 3% and the scatter of r_{av} should be less than 1%, i.e. 0.06 Å. A similar situation obtains if one assumes also a greater scatter of r_{av} but with a sharp extremum at r = 6.2 Å.

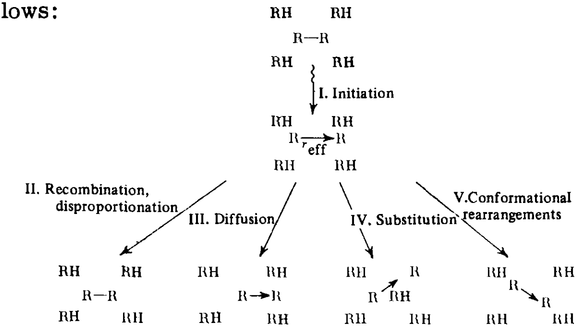
The pairs of iminoxy-radicals arising in dimethylglyoxime single crystals on radiolysis at 77 K have structural parameters close to those in the undamaged structure of the crystal[21]. Even when "large" water molecules are evolved in the formation reaction[50], the scatter of the distances is less than 1%. However, in this case a broad background line is generated and probably includes the spectra of the radical pairs stabilised in the defect regions with several different distances between the radicals, i.e. a distribution with respect to r_{av} with a sharp extremum is observed. In glassy solutions the stabilisation conditions must reflect the inhomogeneity of the matrix structure. Thus the EPR spectra of allowed transitions in frozen solutions of certain acyl peroxides[51] are more broadened, apparently owing to the presence of a distribution with respect to r_{av}. Tetraphenylhydrazine, where radical pairs with fixed distances between the radicals are observed even in frozen solvents, is an interesting example. The sterically branched tetraphenylhydrazine molecules probably generate a solvent structure in their vicinity. On the other hand, in the decomposition of "ribbon" molecules, which generate a solvent structure less effectively, a distribution with respect to r_{av} is generated.

An intermediate case between pair formation in the decomposition of a single molecule, on the one hand, and the formation of pairs from two neighbouring molecules is pair generation from "weak" binary complexes[52]. In this case a rectangular distribution [Eqn. (4)] is observed with respect to the distances between the radicals in the pair with $\Delta r = r_{\max} - r_{\min}$ = 0.2 Å. This feature of pair stabilisation has been used to investigate the geometry of the formation of binary complexes—the precursors of radical pairs. The structure of the binary complex of 3,6-di-t-butyl-*o*-quinone with 2,4,6-tri-t-butylphenol, formed on mixing these compounds, has been determined[22] from the EPR spectra of the radical pairs formed on photolysis. The pair stabilisation conditions determine the stereochemistry and kinetics of thermal radical reactions, which are considered in the next section of the review.

IV. THE KINETICS OF ELEMENTARY REACTIONS IN THE "CAGE"

One of the most significant features of solid-phase reactions is the limited mobility of the reacting species or species formed as a result of the reaction. For this reason, the solid may be represented, with an adequate degree of approximation, as a body consisting of compartments ("cages") containing immediately adjoining molecules; the compartments do not interact with one another and for this reason do not average out the properties of the system. The data at present available for the kinetics of solid-phase radical reactions show that virtually all the characteristics of the processes are already manifested on a scale corresponding to a single cage. A radical pair trapped in the cage serves as the ideal probe for the direct measurement of the kinetic constants of elementary reactions in the solid phase. This section reviews the results of such measurements and discusses certain specific conclusions concerning the mechanisms of solid-phase reactions based on them.

The overall mechanism of processes occurring in the cage on formation of radical pairs can be represented as follows:



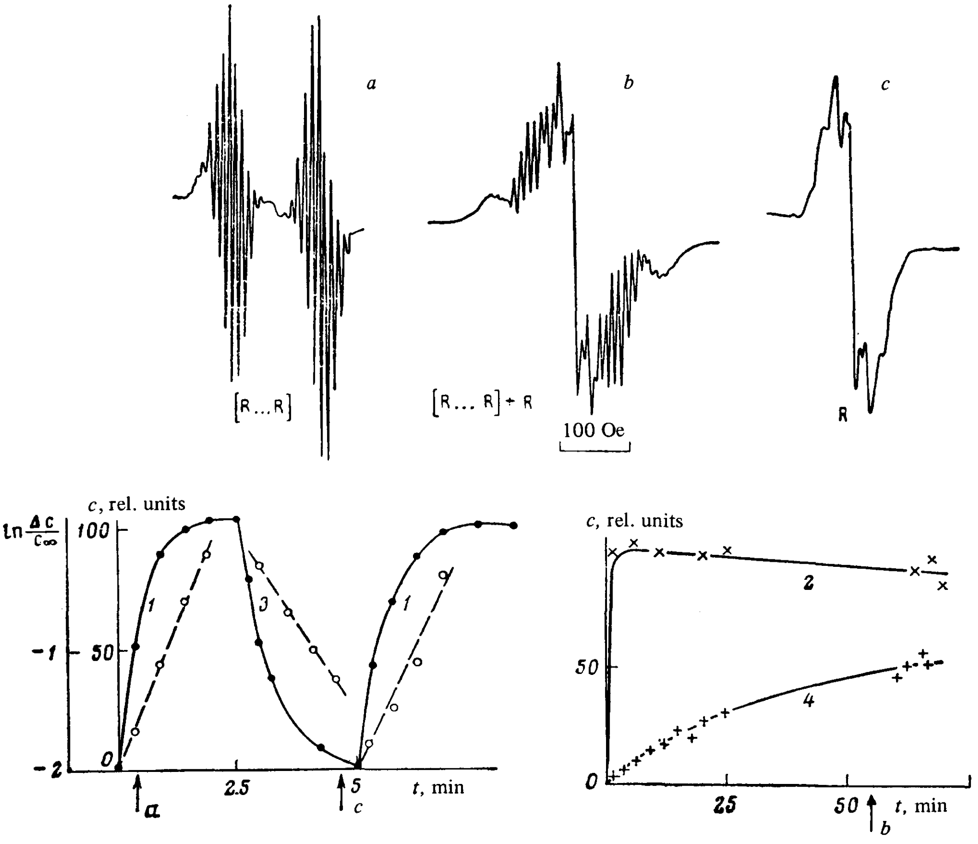


Figure 7. Kinetics of the accumulation (curves *1* and *2*) and destruction (curve *3*) of radical pairs and the accumulation of radicals (curve *4*) in the photolysis of azobisisobutyronitrile at 77 K. The linear forms of the kinetic curves are illustrated by dashed lines in terms of the variables corresponding to an exponential radical destruction law: above—EPR spectra at the instants indicated by arrows on the abscissa axes.

Depending on the ratio of the rate constants for different steps, a particular reaction pathway obtains in each specific system. On photolysis the radical pairs formed largely recombine or disproportionate in the cage and a simplified reaction mechanism can be represented as follows:

$$\begin{tikzcd} M \arrow[r, squiggly, "k_0"] & {[R_1 \ldots R_2]} \arrow[r, "k_2"] \arrow[d, "k_1"'] & R_1+R_2 \\ & M' & \end{tikzcd} \quad . \qquad (5)$$

The radical pairs produced on radiolysis are usually stable at the initiation temperature and on heating it is possible to investigate independently processes II, IV, V. When pairs of stable radicals are used, it is convenient to investigate diffusion processes III.

1. Recombination and Liberation from the Cage

The study of "live" metastable radical pairs, formed on photodecomposition of unstable organic compounds, is of considerable interest for understanding the mechanism of initiation in the solid phase.

On the basis of the simplest mechanism (5) of the photodissociation of molecules in the cage, it is easy to obtain the following expressions from the kinetics of the accumulation of radical pairs (without taking into account the subsequent reactions of isolated radicals):

$$c_{RR} = c_\infty \{1 - \exp[-(k_1+k_2)t]\},$$

$$c_R = \frac{k_2}{k_1+k_2} c_\infty [(k_1+k_2)t - \{1 - \exp[-(k_1+k_2)t]\}], \qquad (6)$$

where $c_\infty = k_0 c_M/(k_1 + k_2)$. It follows from Eqns. (6) that an induction period, approximately equal to the lifetime of radical pairs, should be observed in the accumulation of radicals and that a steady radical accumulation rate should be established subsequently:

$$w_R = k_0 c_M k_2/(k_1+k_2) = f k_0 c_M,$$

where f is the probability of liberation from the cage. Since the initial rate of accumulation of radical pairs $w_{R\ldots R} = k_0 c_M$, it is possible to find the probability of liberation from the cage on the basis of the ratio of the slopes of the linear sections of the experimental curves, while measurements of the absolute rate and the analysis of the radical pair accumulation or destruction curve make it possible to determine all the kinetic constants in Eqns. (5). Experiments of this type have been carried out on the photodecomposition of solid organic initiators—azobisisobutyronitrile,[3,53] azobis-3-methyl-2-phenylbutane,[54,55] tetraphenylhydrazine,[18,24] and a number of acyl peroxides[24,51] At low temperatures (77–100 K, sometimes up to 150 K) EPR spectra can be recorded for crystalline substances and frozen solutions. Some of the results of the kinetic studies are illustrated in Fig. 7. The signal intensities in Fig. 7 are quoted in relative units but account is taken of the shape coefficients of the spectra, so that the values of c_R and $c_{R\ldots R}$ are proportional to the true concentrations. We thus find from Fig. 7 that $f = 2 \times 10^{-2}$ at 77 K for crystalline azobisisobutyronitrile. This value is much less than that obtained from kinetic measurements in solution ($f = 0.5$ according to Kulitski et al.[56]), but is in good agreement with $f = 3 \times 10^{-3}$ calculated for the initiation of polymerisation in the solid phase[57].

Fig. 7 shows that the radical pair accumulation and destruction kinetic curves can be expressed in a satisfactory linear form in terms of semilogarithmic coordinates, i.e. the destruction of radical pairs is indeed a first-order reaction. The rate constant for the destruction of radical pairs in the "cage" in crystalline azobisisobutyronitrile has been measured[58] over the range 63–77 K. Further measurements have been made in tetraphenylhydrazine single crystals. The constants are compiled in the Table.

Kinetic curves for radical pairs and radicals formed in the photolysis of acetylbenzoyl peroxide have been published[51]. The radical accumulation curve shows a distinct inflection associated with the lag in the formation of radicals, in conformity with Eqn. (6). This implies that radical initiation precedes the appearance of isolated (in the given instance methyl) radicals, but the induction period is clearly shorter than the time required for the establishment of a steady-state concentration of radical pairs, i.e. the reaction mechanism is apparently more complex than that described by Eqns. (5).

In the study of processes of the type described the problem naturally arises whether the recombination reactions and the reactions involving liberation from the cage are thermal or whether they are also associated with photoexcitation. In the case of azobisisobutyronitrile the time constants for photoaccumulation and destruction in the dark are the same (Fig. 7), which indicates a thermal mechanism of the recombination reaction. On the other hand, in the case of acyl peroxides, direct data have been obtained indicating the influence of light on the liberation from the cage. For example, when peroxydisuccinic acid is irradiated with light at wavelengths in the range 240 to 400 nm, radicals and radical centres accumulate rapidly, but only pairs are produced in the presence of light corresponding to the 330–570 nm band[51]. The radical pairs in peroxydisuccinic acid are converted into radicals even under the influence of visible light[51]. The kinetics of the destruction of radical pairs formed in the low-temperature photolysis (77 K, 300–400 nm) of mono- and poly-crystalline tetraphenylhydrazine specimens and frozen solutions of tetraphenylhydrazine in toluene have been studied in detail[59,60]. In single crystals the destruction of radical pairs obeys the equation for first-order kinetics. In powders and vitrified solutions the kinetics are of the "stepwise" type, which corresponds to a set of kinetic constants (see Table) with a rectangular distribution with respect to E having a width $\Delta E = 2.3 \pm 1$ kcal mole^{-1} and $\lg k_0 = 12.1 \pm 3$ s^{-1}. Vitrified solutions of tetraphenylhydrazine are interesting in view of the similarity of the experimental conditions to those which really obtain when compounds of this class are used as initiators. It has been shown[60] that the probability of the liberation of radicals from the cage and hence the efficiency of the initiator are negligibly small in the vitrified crystalline state and that the probability is close to unity in the region corresponding to the devitrification of the solution.

In those cases where the reactions take place in the region remote from the phase transition temperatures, the reaction in the cage becomes strongly stereospecific. A set of studies in this field was undertaken by McBride and coworkers[53–55,61]. When asymmetric fragments recombine, the composition of the products is not random but depends on the structure of the cage. Thus in the case of crystalline azobisisobutyronitrile 95% of the photolysis products are formed via radical pairs in undisrupted regions of the crystal and only ~5% may be formed on defects, giving rise to other compounds[61]. In the liquid phase the ratio of product yields is reversed. A study of the photolysis of acetylbenzoyl peroxide has shown that even at low temperatures the products are not just a pair of benzoyloxy- and methyl radicals but also (as a result of decarboxylation) a "phenyl-methyl radical" pair. This gives rise to a large set of recombination products which may be formed in the cage. However, the structure of the cage facilitates the interaction of the methyl radical with oxygen forming part of the peroxide chain before decomposition, which leads to the selective formation of products[51].

2. Substitution and Disproportionation Reactions in the Cage

At low temperatures, where the diffusional mobility of large molecules is frozen, reactions of the type

$$R + RH \rightarrow RH + R, \qquad (7)$$

which are capable of ensuring the migration of the valence over considerable distances, acquire particular importance. Such reactions may occur both on heating and under the influence of light. However, direct measurement of the kinetic constants for reaction (7) became possible only when radical pairs were used, because there is no change in chemical structure during the reaction and only the coordinate of the active centre is altered. Reactions of type (7) were first investigated in detail in γ-irradiated dimethylglyoxime and $\{[D_2]$dimethylglyoxime [31,62]$\}$. The rate constants, the kinetic isotope effects, the direction of migration, and hydrogen migration distances were measured. The experimental results are presented in Fig. 8 and in the Table. A characteristic feature of the thermal valence migration reactions is their stereospecificity—the anisotropy of the directions of valence migration. The sensitivity of reactions to weak intermolecular interactions is a no less interesting feature. Thus it has been observed[31] that at low temperatures (77–120 K) intramolecular migration of hydrogen via one of two pathways, equivalent as regards the direction in the crystal, the distance traversed, and the chemical structure of the radical fragments, is observed. It is apparently due to the ability of iminoxy-radicals to form hydrogen bonds with the molecules of the medium or with one another.

In those cases where there are no interactions of this kind or their energy is low compared with the activation energy for the migration reaction, a dynamic equilibrium is observed between two positions of the active centre. In dimethylglyoxime[31] such migration reactions are observed at higher temperatures (270–320 K). There is intermolecular migration of a hydrogen (deuterium) atom, which can be located in two closely adjacent positions with equal probabilities; this is manifested when the EPR spectra of two types of radical pairs are recorded. A similar behaviour has been observed in studies[30,52] of the photolysis of frozen solutions of 2,4,6-tri-t-butylphenol and 3,6-di-t-butyl-*o*-benzoquinone, which form a weak complex (see Section III). The transfer of a hydrogen atom from phenol to quinone leads to the formation of radical pairs of two types, which arise owing to the intramolecular exchange between the two carbonyl groups of *o*-quinone.

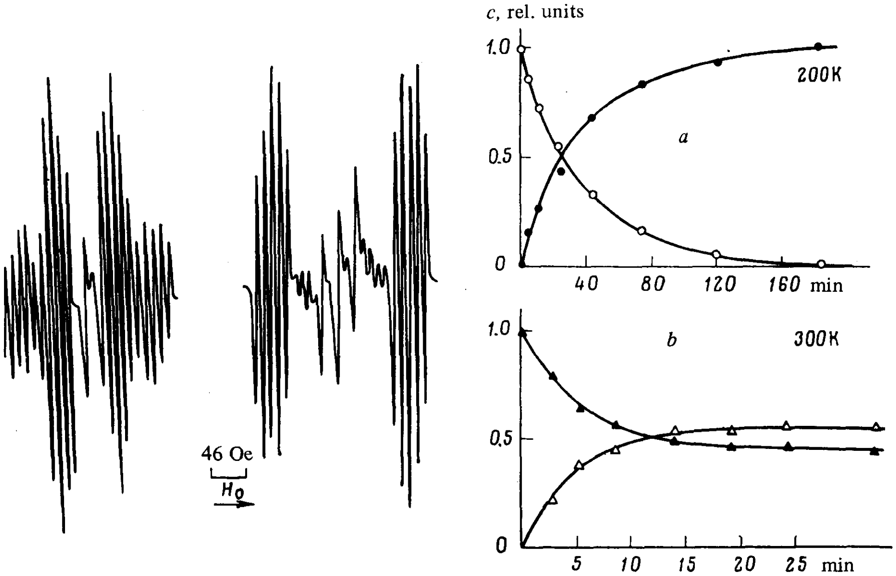
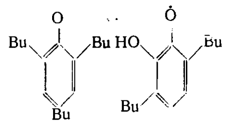
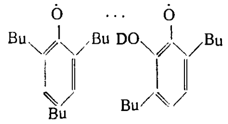
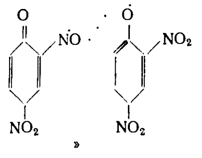
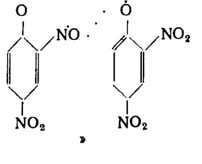


Figure 8. Kinetics of intramolecular (*a*) and intermolecular (*b*) substitution reactions (R...HR) → (RH...R) in γ-irradiated $[D_2]$dimethylglyoxime (*a*) and non-deuterated dimethylglyoxime (*b*): on the left—transformation of the EPR spectra of the radical pairs in the course of the intramolecular substitution[31].

The rate constants for elementary radical processes determined from the EPR spectra of radical pairs.

Structure of radical pair	r_1, r_2, Å	Phase state	Elementary process	Parameters	ΔT, K	Refs.
		Azobisisobutyronitrile				
R...N≡N...R, where $R=(CH_3)_2C(CN)$	$r_1=5.6$	Single crystal	Recombination	$E=3.5\pm0.6$, $\lg k_0=8$	63—77	3
»	$r_1=5.6$	Single crystal	Recombination	$E=5.0$; $\lg k_0=11$	72—77	35
»	$r_1=5.6$	Single crystal	Liberation from cage	$f=(2\pm1)\cdot10^{-2}$	77	3
		Tetraphenylhydrazine				
$Ph_2\dot{N}$ $\dot{N}$	$r_1=4$	Single crystal	Recombination	$E=7.0\pm0.5$; $\lg k_0=8.4\pm0.8$	130—150	59
»	$r_1=4$	Crystallised solution in toluene	Recombination	$E_{min}=5.4\pm1.5$; $E_{max}=7.7\pm2.2$; $\lg k_0=12.1\pm3$	77—130	59
»	$r_1=4$	Vitrified solution in toluene	Recombination	$E_{min}=5.2\pm1.5$; $E_{max}=7.5\pm2.0$; $\lg k_0=11.6\pm3$	77—110	60
»	$r_1=4$	Devitrification region	Liberation from cage	$E\simeq30$; $\lg k_0\simeq70$; $f\geqslant0.1$	110—120	60
		Dimethylglyoxime				
HONPNO$^\bullet$...$^\bullet$ONPNOH, where $P=C_2H_2(CH_3)_2$	$r_1=5.4$ $r_2=5.5$	Single crystal	RH+R→R+RH	$E=1.40\pm0.07$; $\lg k_0=0.10\pm0.16$	77—110	31
DONPNO$^\bullet$...$^\bullet$ONPNOD	$r_1=5.4$ $r_2=5.6$	Single crystal	RD+R→R+RD	$E=7.4\pm0.1$: $\lg k_0=4.5\pm0.1$	190—200	31,62
HONPNO$^\bullet$...$^\bullet$ONPNOH	$r_1=5.6$ $r_2=6.1$	Single crystal	$RH+R\underset{k_{21}}{\overset{k_{12}}{\rightleftarrows}}R+RH$	$E=17.7\pm0.7$; $\lg k_0=10.5\pm0.6$; $k_{12}/k_{21}=1.4\pm0.2$	270—310	31,62
DONPNO$^\bullet$...$^\bullet$ONPNOD	$r_1=5.6$ $r_2=6.1$	Single crystal	$RD+R\underset{k_{21}}{\overset{k_{12}}{\rightleftarrows}}R+RD$	$E=24.2\pm0.4$; $\lg k_0=13.2\pm0.3$; $k_{12}/k_{21}=1.4\pm0.2$	310—340	31,62
HONPNO$^\bullet$...$^\bullet$ONPNOH	$r_1=5.6$ $r_1'=6.1$	Single crystal	Disproportionation	$E=21.5\pm0.9$; $\lg k_0=10.8\pm0.6$	30[illegible]40	31,62
DONPNO$^\bullet$...$^\bullet$ONPNOD	$r_1=5.6$ $r_1'=6.1$	Single crystal	Disproportionation	$E=22.1\pm0.9$; $\lg k_0=11.3\pm0.6$	300—340	31,62
		Complex of 2,6-di-t-butyl-*o*-benzoquinone and 2,4,6-tri-t-butylphenol				
	$r_1=5.15$ $r_1'=6.25$	Vitrified solution in liquid paraffin	Disproportionation	$E_{min}=6.7\pm1$; $E_{max}=10\pm1$; $\lg k_0=8\pm2$	130—200	52
	$r_1=5.15$ $r_1'=6.25$	Vitrified solution in liquid paraffin	Disproportionation	$E_{min}=11\pm1$; $E_{max}=17\pm1$; $\lg k_0=13\pm2$	130—200	52
		2,4-Dinitrophenol (OH)–2,4-dinitrophenol (OD)				
	$r_1=5.18$ $r_2=4.8$	Polycrystalline substance (OH)	Rearrangement of CNO fragment	$E=9.4\pm0.2$; $\lg k_0=8.7\pm0.2$	160—190	81
»	$r_1=5.18$ $r_2=4.8$	Polycrystalline substance (OD)	Rearrangement of CNO fragment	$E=9.5\pm07$; $\lg k_0=8.1\pm0,8$	160—190	81
»	$r_1=4.8$ $r_2=4.68$	Polycrystalline substance (OH)	Rotation of radical as a whole	$E=9.8\pm1.5$; $\lg k_0=6.6\pm1.6$	200—240	81
»	$r_1=4.8$ $r_2=4.68$	Polycrystalline substance (OD)	Rotation of radical as a whole	$E=9.7\pm1.3$; $\lg k_0=6.7\pm1.3$	200—240	81
	$r_1=4.68$	Polycrystalline substance (OH)	Recombination	$E_1=18.7\pm0.8$; $\lg k_{01}=12.0\pm0.6$ $E_2=22.4\pm0.5$; $\lg k_{02}=13.4\pm0.5$	270—310	81
»	$r_1=4.68$	Polycrystalline substance (OD)	Recombination	$E_1=27.5\pm2.5$; $\lg k_{01}=17.2\pm1.9$ $E_2=29.6\pm6.5$; $\lg k_{02}=18.3\pm4.8$	270—310	81

Notation: r_1 and r_2 are the distances between the radicals before and after the process, E (kcal mole^{-1}) and k_0 (s^{-1}) are the Arrhenius parameters of the rate constant, f is the probability of liberation from the cage, ΔT is the temperature range, and E_1, k_{01}, E_2, and k_{02} are the parameters for low and high degrees of conversion respectively.

Under the influence of ultraviolet light, migration reactions are also observed in γ-irradiated dimethylglyoxime crystals at 77 K.[63] However, they are non-stereospecific and proceed via several pathways simultaneously. Irradiation with light apparently leads to electronic excitation of the radicals, which react in the excited state either with a neighbouring radical (destruction of the pair) or with a neighbouring molecule (valence migration).

Disproportionation reactions have much in common with valence migration reactions of type (7). As a rule, they exhbiit a kinetic isotope effect[31,52,62]. The stereochemistry of the disproportionation of radical pairs has been examined[57] and it has been shown that the pathway followed in the transfer of hydrogen from the quinone radical to the phenone radical during "annealing" does not coincide with the channel in phototransfer or during formation. The rate of reaction is then extremely sensitive to the distance traversed and a distribution with respect to distances leads to a distribution with respect to rate constants.

3. Characteristics of the Kinetics of Elementary Reactions in the Cage

The kinetic constants found from the EPR spectra of the radical pairs are compiled in the Table. Evidently even in those cases where the reaction is elementary, i.e. the kinetics satisfy a first-order equation, the Arrhenius parameters differ sharply from the "usual" values for analogous reactions in the gas and liquid phases. In vitrified and powdered matrices the reaction kinetics are "polychromatic" and are described by a spectrum of kinetic constants. These features are in general characteristic of the kinetics of radical reactions in solids[59,64-67] and are apparently of key importance for the understanding of their mechanism. For radical pairs, it is possible to achieve the closest approach to the elementary stages of the process. It will be shown below that in many instances this has made it possible to understand the nature of the observed phenomena.

Tunnel transfer of hydrogen. From the kinetic point of view, rapid thermally activated migration reactions, occurring in dimethylglyoxime at low temperatures, are of particular interest. The measured dependence of the rate constants on temperatures obeys the Arrhenius equation. However, the pre-exponential factors for unimolecular reactions vary over a wide range, from several reciprocal seconds (for a reaction at the temperature of liquid nitrogen) to normal values of 10^{13} s^{-1} at 300 K, and there is a linear compensation relation between $\lg k_0$ and E. The migration reactions investigated are characterised by considerable kinetic isotope effects. Low pre-exponential factors for the low-temperature reactions and the anomalously large kinetic isotope effect indicate a tunnel reaction mechanism. If the rate of the process is estimated in terms of the reaction [RH...R] → [R...HR] for a continuous distribution of the vibrational levels of the bond being ruptured, then the experimental points corresponding to a barrier half-width $d_{1/2}$ = 0.6 Å, E_H = 15 kcal mole^{-1}, and E_D = 16 kcal mole^{-1} fit satisfactorily on theoretical curves (Fig. 9). In order to illustrate the relation between the true and apparent activation energies, "Arrhenius" straight lines have been drawn through the experimental rate constants in Fig. 9. Evidently the unjustified linear extrapolation yields in this case unduly low values of E and k_0 and for deuterated dimethylglyoxime higher pre-exponential factors correspond to higher values of E, i.e. a compensation effect is observed. Subsequently the occurrence of hydrogen transfer via a tunnel mechanism at low temperatures was confirmed by numerous experimental investigations (see the review of Lebedev et al.[69]).

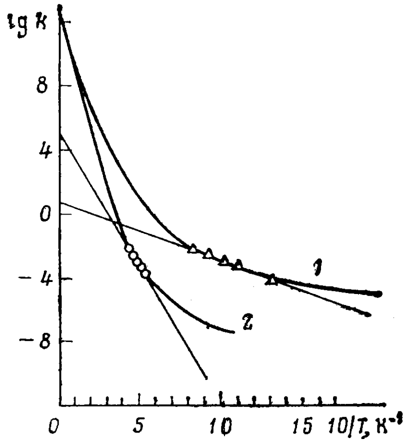


Figure 9. Calculated and experimental temperature dependences of the rate constants for the reaction (R...RH) → (RH...R) in dimethylglyoxime (curve *1*) and [D$_2$]dimethylglyoxime (curve *2*). The calculation was carried out taking into account the tunnel transitions for the quasi-continuous distribution of the vibrational levels of the dissociating bond corresponding to a barrier half-width $d_{1/2}$ = 0.6 Å and barrier heights E = 15 and 16 kcal mole^{-1} respectively[62]. Evidently in the temperature range of the measurement it is possible to draw straight lines through the experimental points, whose slope yields the apparent activation energy $E_{\text{eff}} \ll E$.

Polychromatic reactions. In most radical reactions occurring in the solid phase at low temperatures, a kinetic arrest of the reaction (i.e. a sharp reduction of its rate) is observed for a certain degree of reaction. The stepwise nature of the recombination is usually accounted for by the fact that the reacting centres are non-equivalent and that a set of reaction rates obtains. Several hypotheses explaining such distribution of properties have been put forward[64-67,69]: (a) structural inhomogeneity of the specimen; (b) the presence of a distribution with respect to the distances between the reacting species; (c) an increased local concentration of radicals at the sites of defects; (d) thermal chain recombination†. The last two possibilities are known to be negligible for radical pairs. The distribution of properties in the case under consideration may be due either to the structural inhomogeneity of the specimen or to the stabilisation of radicals separated by different distances.

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†Thermal chain recombination is the chain destruction of free radicals activated by the energy liberated in the elementary recombination step.

A correlation has been observed[34] between the distance in the radical pair obtained on γ-radiolysis of $C_{10}D_{22}$ and their destruction temperature. It has been possible to establish directly[52] the relation between the rate constant (activation energy) for the reaction and the distance between the reacting radicals in the cage. In frozen solutions of quinones and phenols a change in the parameter D, i.e. in the distance between the radicals, was observed in the course of the stepwise "annealing" of radical pairs, associated with the disproportionation of radicals in the cage. An increase of D by 0.2 Å corresponded to an increase of the activation energy for the reaction by 3.3 kcal $mole^{-1}$. In polycrystalline n-decane the variation of the distance between the radicals in the course of their recombination was investigated by the method involving the saturation of forbidden transitions (Fig. 10). It has been shown[36] that the activation energy for recombination increases approximately linearly with distance in the range 6–8 Å.

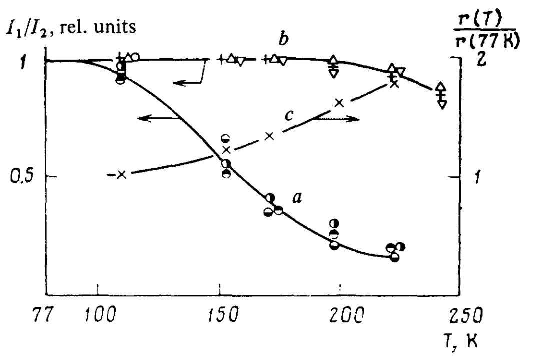


Figure 10. "Annealing" of the EPR signals of radical pairs (a) and isolated radicals (b) in γ-irradiated polycrystalline n-decane; c) variation of the minimum distance between the radicals during "annealing". Analysis of curves a and b shows that the effective activation energy for the recombination reaction increases linearly with distance[36].

However, the scatter with respect to distances is not the only cause of the existence of a set of rate constants for the reaction in the cage. In many instances the stepwise reaction is not accompanied by a change in the parameter D. This implies the existence of kinetically non-equivalent cages owing to a difference in the immediate environments of the reacting molecules. The direct influence of the inhomogeneity of the matrix on the reaction kinetics has been demonstrated[67,70]. It has been shown that in oriented polyethylene the kinetics of the destruction of a radical pair with r_{av} = 5.3 Å, studied on the basis of the spectrum of an allowed transition, are distinctly "stepwise" and the scatter of the constants is very wide. This observed feature has been followed consistently in experiments using tetraphenylhydrazine[59,60] where the recombination of pairs with the same distances between the radicals in single crystals obeys a simple first-order law, while in vitrified and crystallised solutions and in crystalline tetraphenylhydrazine powder the destruction kinetics become stepwise (Fig. 11). The results described demonstrated probably for the first time that the stepwise kinetics of solid-phase reactions are due to the scatter of the properties of the medium at the level of the kinetic cage.

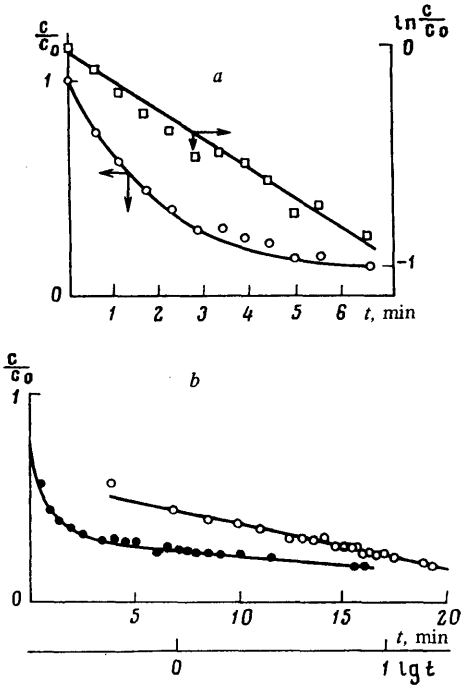


Figure 11. Kinetics of the "merging" of the radical pairs in single crystals (a) and in a polycrystalline solution of tetraphenylhydrazine in toluene (b). In the former case the kinetic curve is described by an exponential function and in the latter by a linear relation with lg t, which indicates the existence of a broad spectrum of rate constants[59].

The existence of cages with different immediate environments in vitrified solutions is not particularly surprising. However, the stepwise nature of the destruction of radical pairs in powdered specimens requires special consideration. The four types of radical pairs formed in the decomposition of four molecules with different orientations are magnetically non-equivalent in tetraphenylhydrazine crystals. In polycrystalline specimens the pairs are spectroscopically identical, but the exponential kinetics of the destruction of radical pairs of each type are characterised by different rate constants[59]. By measuring the overall concentration of pairs of all types, we can observe complex first-order kinetics—stepwise destruction. An analogous behaviour has been observed in the "annealing" of radical pairs in 2,4-dinitrophenol. Analysis of the spectra revealed two sets of magnetically non-equivalent radical pairs and the destruction kinetics in powders became satisfactorily linearised on the assumption that there are two exponential destruction rate constants. Thus the EPR spectra of radical pairs in crystalline solids allow the resolution of kinetically non-equivalent states of radical pairs (with a fixed distance). This makes it possible to investigate the relation between the structure of the cage and its dynamic properties.

V. CONFORMATIONAL AND MOLECULAR MOBILITY IN SOLID MATRICES

The data described above confirm that the reactions in solid matrices are controlled by or at least depend strongly on molecular motions in the cage. For this reason, the simultaneous investigation of elementary molecular motions (translational displacement, rotation, reorientation, and conformational rearrangements) and chemical reactions is a very important task. The spin probe method[71–73] is not very effective for such purposes, since in most cases the reactions are "unfrozen" at very low frequencies of molecular motions when the EPR spectra of the paramagnetic label of the probe do not yet show any changes. The recombination-kinetic method[65] permits the detection of slow molecular motions but it yields only indirect information about the elementary motions, since it is based on the measurement of the rate of the overall recombination of radicals. The use of radical pairs as two-spin probes in the matrix leads to the possibility of the direct investigation of the dynamics and stereochemistry of slow molecular motions.

1. The Study of Phase and Structural Transitions

For compact radical pairs, the recombination of active centres does not require translational diffusional displacements and pair labels are presumably extremely sensitive to local molecular motions. It has been shown[74] that the different stabilities of radical pairs in polymers are of interest from the standpoint of the detection of phase and structural transitions (Fig. 12). Fig. 12 shows that the heating curve for $\Delta M_S = 2$ signals has inflections indicating structural changes in the polymer, i.e. phase transitions slightly "modulate" the curve for the distribution of the pair recombination activation energies. Inferences can be drawn about the structural and phase transitions by measuring the distances between the radicals r_{av} over a wide range of temperatures for any type of pairs which are stable at high temperatures. In the absence of transitions a dependence reflecting simply the linear expansion of the crystal will be obtained[75].

2. Translational Mobility

The frequency of translational motion can be determined directly from the EPR spectra of radical pairs because the liberation of the radical from the cage and its migration over a distance corresponding to one cage diameter lead to the disappearance of the spectrum of the radical pair and to the appearance of signals due to the isolated radicals. The kinetics of the liberation of the diphenylnitrogen radical from the cage have been investigated[60] for the devitrification of frozen solutions in toluene. The characteristic times of the liberation of the radical from the cage $\tau \simeq 10$ s makes it possible to estimate the frequency of translational motion in the liquid phase $\nu_{tr} \gtrsim 10^{-1}$ s^{-1}. To refine the estimate, the EPR spectra of frozen solutions of the stable 2,2,6,6-tetramethyloxopiperidin-1-yloxy-radical in toluene were recorded. Since a change in the form of this spectrum was not observed on devitrification, the upper limit to the rotational frequency is $\nu_{tr} < 10^8$ s^{-1}.

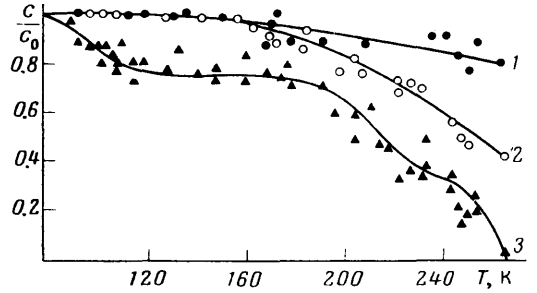


Figure 12. Heating curves for alkyl radicals (curve *1*), a mixture of alkyl and peroxy-radicals (curve *2*), and radical pairs (curve *3*) in polyethylene. The inflection points in the range 160–260 K correspond to structural transitions in the crystalline phase[74].

Yet another interesting possibility of investigating elementary translational motions arises when one employs the stable radical pairs formed as a result of the random entry of radicals into a single cage on dissolution of nitroxy-radicals at high concentrations (0.01–0.1 M).[76] The $\Delta M_S = 2$ transitions at half field (see Section II) are then distinctly observed despite the existence of a more intense $\Delta M_S = 1$ signal due to the isolated radicals.

When the translational mobility is "unfrozen", the number of pairs of chemically stable radicals remains unchanged and is statistically determined, though the lifetime of an individual pair diminishes, since it is determined by the average residence time of the radical in a "settled" position, i.e. the correlation time for translational motion τ_{tr}. This leads to the modulation of the values of r_{av} and α, and, in conformity with Eqn. (2), to the modulation of the intensity of the $\Delta M_S = 2$ transition with a frequency τ_{tr}^{-1}. As a result, the EPR line should become broadened by an amount $1/\gamma_{tr}$, i.e. it becomes possible to measure the frequencies of the translational jumps executed by the radical[76]. A rigorous calculation of the line form fully confirmed this simple picture[77].

A study has been made[76] of the EPR spectra of solutions of 2,2,6,6-tetramethylpiperidinyl-1-oxy-radicals in liquid paraffin and toluene at a concentration of (1–5 (1–5) $\times 10^{19}$ cm^{-3}. The temperature variation of the EPR signal is illustrated in Fig. 13. Evidently the intensity of the forbidden transition diminishes, but the line width hardly increases. Such behaviour of the line cannot be accounted for within the framework of relaxation theory[77] and indicates the existence of a set of very different frequencies of translational motions τ_{tr}^{-1}. In this case the $\Delta M_S = 2$ signal represents, as it were, a superposition of lines with very different widths; only the narrowest line, corresponding to the signal due to cages where the jump frequency is a minimum, is recorded. Thus polychromatic kinetics are characteristic not only of chemical reactions but also of elementary motions in the solid. This agrees well with the model of kinetically non-equivalent cages, which is nowadays resorted to for the interpretation of a wide variety of processes in the solid phase[65-67,69].

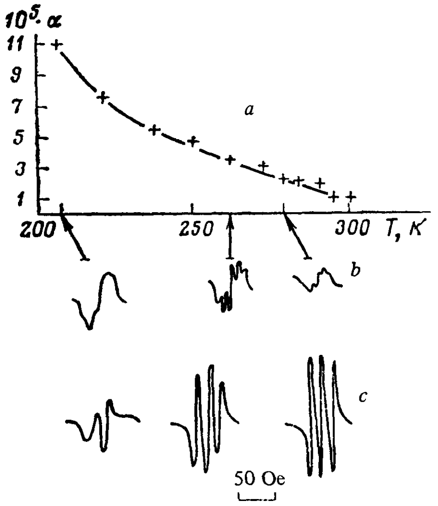


Figure 13. Temperature dependence of the relative intensity (*a*) and form of the EPR spectrum (*b*) for the $\Delta M_S = 2$ transition involving stable radical pairs in liquid paraffin; *c*) EPR spectra of single crystals ($\Delta M_S = 1$). The decrease of the $\Delta M_S = 2$ signal intensity without an increase in line width indicates the presence of a broad spectrum of frequencies of the translational displacements of radicals[76].

3. Rotational Mobility

If a two-spin system is sufficiently rigid (biradicals, triplet molecules, radical pairs formed from complexes), then effects completely analogous to those described above will be observed as a result of rotational mobility[76]. The orientational spin probe method is of particular interest in this instance[78]. Signals due to species where the tensor axis D is oriented mainly in one direction can sometimes be isolated with the aid of the magnetophotoselective effect described in Section III or as a result of strong magnetic fields[79]. This makes it possible, in principle, to investigate the kinetics of the rotational disorientation of species with very long correlation times[76]. Measurements performed by this method have also shown that, in vitrified solutions and in polymers, the rotational motions of molecules are polychromatic, i.e. take place with different frequencies in different cages. One of the important problems which investigators have attempted to solve in this manner consists in the choice between two types of elementary motion: rotation in very small random jumps (rotational diffusion) or rotation in large non-correlation jumps. Two different models of elementary processes in the solid phase correspond to these two types of motion: the quasi-crystalline and free-volume models[80]. However, it has not so far been possible to make a final choice (based on experimental data).

4. Conformational Rearrangements

Since the orientation of the reactive groups in molecules is specified by the matrix structure, the study of the dynamics of intra- and inter-molecular rearrangements in the crystal is an essential stage in the investigation of the mechanisms of elementary solid-phase reactions. Fundamentally new possibilities arise in the study of the EPR spectra of radical pairs. In this case the second radical plays the role of a paramagnetic label and a change in the orientation of the radical (or its fragment) leads to a change in the radius-vector of the radical pair r_{eff} and to a marked alteration of the magnetic parameters of the EPR spectrum.

We investigated in detail the structural transformations of iminoxy-radicals in a γ-irradiated 2,4-dinitrophenol matrix at 77 K (Fig. 14),[41,81] and showed that radicals and radical pairs are formed in non-equilibrium conformations with different magneto-relaxation characteristics and thermal stabilities. When the specimens are heated, structural relaxation of two types is observed. In the first, structural transition, there is an appreciable change in the geometry of the CNO fragment due to the difference between the C–N–O angles in the nitrophenol molecule and the iminoxy-radical. The hyperfine interaction constants are also altered and two types of radical pairs are formed with $r_{\text{av}} = 4.8$ Å, differing in the orientation of the inter-electron vector in the cell by 5°. On further heating, the radical changes its orientation in the crystal cell slightly, the structure of the fragment being retained. The kinetics of the structural transitions in radicals are consistent with a first-order reaction. The reactive groups are displaced abruptly over small distances (~0.2 Å). The rearrangements give rise to structurally non-equivalent states, which affects the kinetics of the recombination of radicals in the pairs. The kinetics are more complex—the kinetic curve for powders can be fitted by two exponential functions (see Table).

Thus even a small difference in the structure causes a marked alteration of the recombination rate constant. This characteristic is of interest primarily because the occurrence of a large number of intermediate elementary rearrangements can be the reason for the polychromatic kinetics of the recombination reactions. A characteristic feature of the processes investigated is the presence of kinetic isotope effects in the entire chain of transformations, although conformational transitions and recombination involve radicals which do not contain H or D. This demonstrates the major role of the matrix and particularly of hydrogen bonds in the mechanism of radical reactions in 2,4-dinitrophenol. Thus, when the hydroxyl proton is replaced by a deuteron, the rate of the second transition, consisting in the rotation of the molecule as a whole, increases. This may be accounted for by a decrease of the stability of the crystal in parallel with the decrease of the energy of hydrogen bonds when a hydroxyl hydrogen atom is replaced by a deuterium atom in the nitrophenol. The large isotope effect in the recombination reaction (see Table) may be caused by the formation of intermediate complexes of the radicals with the water molecule evolved on radiolysis and captured by the matrix.

The existence of a definite analogy between the conformational relaxation processes considered here and the mechanism of the functioning of complex molecular systems (protein enzymes) is noteworthy[82]. For protein enzymes, it is assumed that, after the formation of a substrate-enzyme complex, rapid relaxation of the active centre takes place directly and is followed by a slow relaxation of the macromolecule. Presumably the behaviour of the hydrogen-bonded molecules in the nitrophenol crystal is to some extent analogous to that of protein macromolecules. Since a molecular crystal is a significantly simpler system than protein, it is possible to interpret in detail the relaxation transitions in this instance.

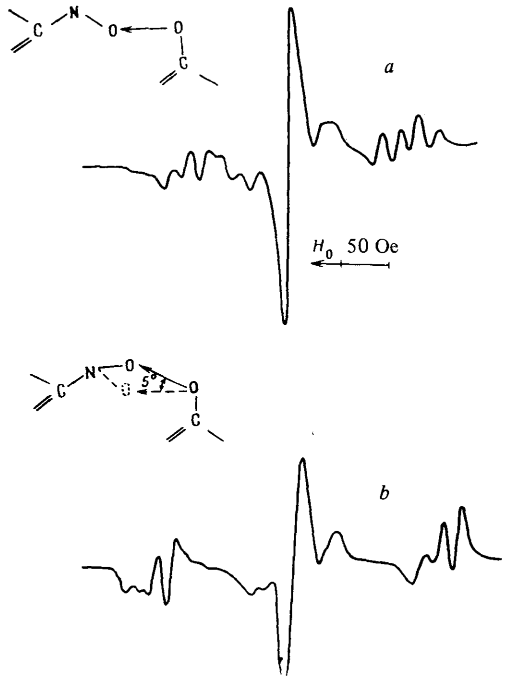
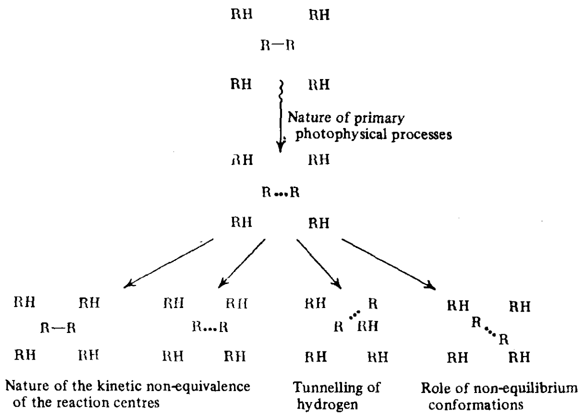


Figure 14. Variation of the EPR spectrum of the "iminoxy–phenoxy"-radical pair in γ-irradiated 2,4-dinitrophenol due to the relaxation of the structure of the CNO fragment. Spectra *a* and *b* were recorded at 77 K and after heating for 10 min at 190 K respectively. Their interpretation is analogous to that illustrated in Fig. 3. In spectra *a* and *b* the C–N–O angle corresponds to the structure of the undamaged molecule and to the equilibrium structure of the iminoxy-radical respectively[81].

oOo

During the decade since the detection of metastable radical pairs, kinetic studies in this field have greatly extended our ideas about the physicochemical foundations of the kinetics of solid-phase reactions. On the basis of the reaction scheme presented at the beginning of Section IV for radical pairs, the most important results of this research can be formulated as follows:



We believe that the demonstration of the kinetic non-equivalence of radicals at the level of the cage, the demonstration of the role of tunnel transitions and conformational changes in solid-phase reactions, and the development of methods for the investigation of the "stereometry of reactions", based on the unique sensitivity of the EPR spectra of radical pairs to changes in the inter-radical vector, are of greatest value. One may hope that further studies in these fields will help to formulate the fundamental characteristics of chemical processes in solid organic substances at least at the level already attained for reactions in the gas phase and dilute solutions.

A completely new field in research on short-lived radical pairs has been initiated recently[83,84]. The results of the latest studies on the structures and spectroscopy of radical pairs, which were not specially considered in this review, may be found in other publications[85-92].

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Dynamics of Degenerate Tautomerism in Free Radicals

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The theoretical principles of the application of the EPR method in the study of the kinetics of exchange processes involving free radicals and radical-anions are described and the results of studies by the EPR method of the tautomeric transformations in radicals and radical-anions, accompanied by the migration of atoms, cations, and organic and organoelemental fragments, are examined.

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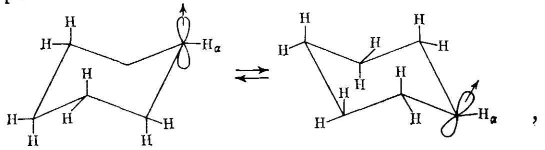
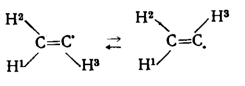
I. INTRODUCTION

In the present review an attempt is made to survey the results of kinetic studies by the EPR method of tautomeric transformations in free radicals and radical-anions or more precisely the reversible intramolecular migrations of atoms and organic or organoelemental fragments between equivalent (or almost equivalent) positions in the molecule and of the cations in pairs formed with radical-anions. Such migration is accompanied by a synchronous redistribution of the unpaired electron density, which leads to a change in the EPR spectra of the species investigated. The application of the EPR method to the study of phenomena of this kind is based on the analysis of the line width in the hyperfine structure (HFS) of the EPR spectra, which frequently proves to be extremely sensitive to changes in the rates of tautomeric transitions. When applied to such processes, the EPR method provides unique possibilities for the investigation of the kinetics of many rapid transitions, the characteristic times of which are in the range between 10^{-6} and 10^{-10} s. There are several types of effects leading to a change in line width, but, for the problems discussed in this review, the most valuable information can be obtained by analysing the so called alternation of line widths in EPR spectra. This effect was observed in 1962 by Bolton and Carrington[1] and independently by Freed and Fraenkel[2]. In the Soviet Union, one of the first investigators to understand this phenomenon was V.V.Voevodskii, under whose supervision research was carried out at the beginning of the 1960s on the inversion isomerisation of the cyclohexyl radical of the chair–chair type[3]:



the *cis–trans* isomerisation of the vinyl radical[4]:



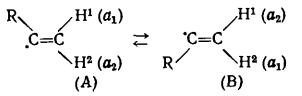
and the delocalisation of the unpaired electron in bridged radical-anions[5] $[\mathrm{Ar{-}X{-}Ar}]^{\overline{\cdot}}\mathrm{M}^{+}$. By analysing the alternation of line widths, it is possible to obtain extremely valuable information about the kinetics of various processes with participation of paramagnetic species. During recent years the method of analysis of line widths in EPR spectra has been closely applied in the study of processes such as the isomerisation of radicals, conformational transitions, electron and proton exchange reactions, and the tautomerism of free radicals and radical-ions.

Before discussing the results of these studies, we shall consider briefly the theoretical principles of the application of the EPR method to the study of the kinetics of exchange processes involving free radicals.

II. THEORETICAL PRINCIPLES

1. Qualitative Considerations

The alternation of line widths in EPR spectra is interpreted on the hypothesis that the hyperfine interaction (HFI), caused by some intermolecular or intramolecular processes, is modulated. We shall consider initially the simplest case where the radical contains only two nuclei with a spin $I = 1/2$. As an example we shall consider the vinyl radical:



Suppose that the HFI constant $a_2 > a_1$. If the radical does not isomerise or the rate of isomerisation is very low, the EPR spectrum corresponds to the picture presented in Fig. 1*a*, where the positions of lines relative to the centre of the spectrum and the spin states of the protons H^1 and H^2 are represented in a conventional manner.

We shall examine the change in the spectrum with increase of the rate of mutual transitions between forms (A) and (B). At first sight, it may appear that both forms of the radicals are identical and therefore there should be no change in the spectrum on transition from one form to the other. However, when account is taken of the spin state of the protons, this is not found to be the case. On passing from form (A) to form (B), the constants a_1 and a_2, corresponding to HFI with the H^1 and H^2 protons in the initial form, correspond in form (B) to HFI with the H^2 and

H^1 protons or, in other words, the protons as it were change places. If the constants a_1 and a_2 in the expressions $\pm\frac{1}{2}(a_2 \pm a_1)$, which characterise the positions of the lines in the spectrum, are made to change places, then it is readily seen that the extreme lines remain in the same positions, while the inner, central components change places or frequency exchange is said to take place. From this very simple picture follows a very important rule, according to which only lines corresponding to identical overall projections $[M_I(H^1) + M_I(H^2)]$ of proton spins undergo frequency exchange.

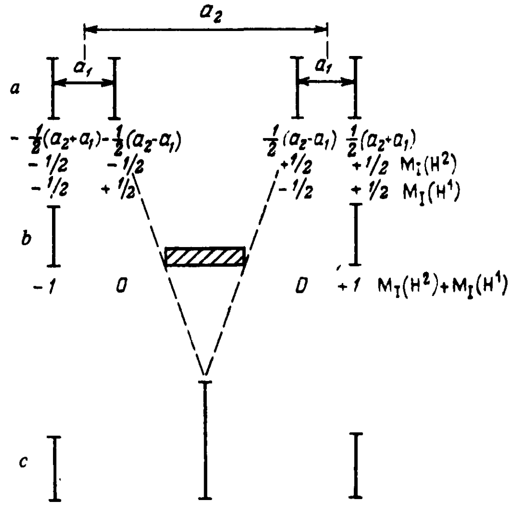
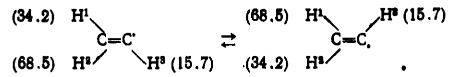


Figure 1. Schematic illustration of the EPR spectrum of an R-substituted vinyl radical: *a*) slow exchange; *b*) intermediate exchange; *c*) fast exchange.

If the rate of isomerisation is not too high, such frequency exchange leads to the broadening and merging of the central components, which is indicated in Fig. 1*b* by the shaded rectangle. In the limiting case of rapid exchange so-called exchange narrowing takes place and the spectrum consists of a triplet with intensity ratios of 1 : 2 : 1 (Fig. 1*c*). A necessary condition for the above picture of the changes in the EPR spectrum as a function of the frequency of the isomeric transition to be valid is antiparallel changes in the two HFI constants a_1 and a_2, i.e. it is necessary that they should be anticorrelated. Indeed this condition holds for the given radicals. While HFI with the H^1 proton becomes more intense, that with the H^2 proton is weakened. As we shall see subsequently, this situation is very frequently encountered in practice.

On the basis of the behaviour of the EPR lines, analysed above, in the spectrum of an R-substituted vinyl radical, it is easy to understand the variations in the EPR spectrum of the unsubstituted vinyl radical under different conditions in the recording of the spectrum. If the radical is obtained at 77 K by the reaction of a hydrogen atom with acetylene[4], an eight-line spectrum (illustrated in Fig. 2*a*) is observed, in agreement with the hypothesis that there are three non-equivalent HFI constants: a_2 = 68.5 G, a_1 = 34.2 G, and a_3 = 15.7 G.



If the same radical is obtained in the liquid phase[6], then the spectrum shows only four lines corresponding to the extreme lines of the low-temperature spectrum. Such transformation of the spectrum can be understood if it is assumed that the two isomeric forms of the radical are involved in rapid interconversion in solution, which leads to the antiparallel modulation of the HFI constants for the H^1 and H^2 protons. For the radicals where the orientations of the nuclear spins of the H^1 and H^2 protons are the same ($\alpha_1\alpha_2$ or $\beta_1\beta_2$), the transition from one tautomeric form to another does not entail a line shift, and for this reason the extreme lines remain narrow. The lines corresponding to the $\alpha_1\beta_2$ or $\beta_1\alpha_2$ state will be displaced and, for a certain rate of transformation, may become broadened to such an extent that they cannot be observed at all (Fig. 2*b*).

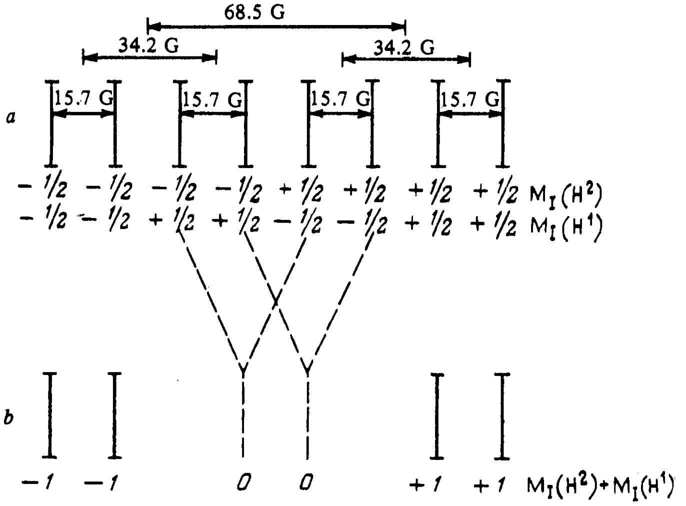


Figure 2. The influence of the rapid interconversion of the tautomeric forms of the vinyl radical on the EPR spectra at 77 K: *a*) spectrum of the radical in a rigid matrix; *b*) spectrum of the radical in the liquid phase.

2. Relation Between Line Width and Kinetics of the Exchange

The graphical description of the broadening of certain components of the EPR spectrum discussed above provides a clear qualitative picture of the influence of transitions between tautomeric forms of the radical on the spectrum. The quantitative relation between the broadening of the components and the frequencies of the intramolecular transformations, on the basis of which it is possible to obtain detailed kinetic information, is examined below.

It is possible to distinguish two main types of effects determining line width: effects associated with the lifetime of the given spin state and effects leading to the fluctuation of the energies of these states. Effects of the first type are determined by the characteristic spin–lattice relaxation time T_1 and those of the second type are determined by the spin–spin relaxation time T_2'. In chemical applications it is reasonable to restrict the treatment to the line widths determined by the reciprocal of the time T_2, which is related to T_1 and T_2' as follows:

$$\frac{1}{T_2}=\frac{1}{T_2'}+\frac{1}{2T_1}. \tag{1}$$

The main task of the theory is to find a quantitative relation between line width $(1/T_2)$ and the kinetic parameters of radical exchange reaction. There are two fundamental approaches to this problem. According to the first, the changes in line width as a result of chemical exchange processes can be described with the aid of modified Bloch equations[7,8], which make it possible to describe the spectra over a wide range of exchange frequencies—from the fully averaged spectrum to the spectrum corresponding to two individual forms of the radical. The second approach, based on the analysis of the relaxation matrix[9], yields a satisfactory agreement with experiment only at high frequencies. We shall consider further the main corollaries arising from the solution of the modified Bloch equations, which are necessary for the interpretation of the experimental data.

The physical significance of the broadening of the lines in EPR spectra is that the reciprocal transitions of the radical from one form to the other alter the local fields in which the unpaired electron is located, which entails a shortening of T_2 and a broadening of the corresponding lines.

Consider a free radical which may exist in two different forms A and B to which correspond different EPR spectra. We shall assume for simplicity that the concentrations of the two forms are identical and that only one EPR line corresponds to each. If there is exchange between forms A and B in this system, the spectrum will depend significantly on the rate of the exchange process, or, in other words, on the lifetimes of forms A and B. The theory usually involves the time τ which is related to the average lifetimes τ_A and τ_B in the following manner:

$$\tau=\tau_A\tau_B/(\tau_A+\tau_B). \tag{2}$$

It is seen from this expression that, when $\tau_A=\tau_B$, the average lifetime of each form, A or B, is 2τ. It is usual to divide exchange processes into three main types depending on their rates: slow exchange, rapid exchange, and intermediate exchange. We shall consider the theoretical form of the spectrum for each specific case.

(a) Slow exchange. If the rate of interconversion of forms A and B is low, then τ is large compared with the difference between the resonance frequencies $(\omega_A-\omega_B)$, and the spectrum consists of two individual signals with an intrinsic width $1/T_{2,0}$ (Fig. 3*a*). With increase of the rate of interconversion, both components are broadened, the broadening in the case of slow exchange being related to the lifetime τ in the following manner:

$$\Delta(1/T_2)=1/2\tau\gamma_e, \tag{3}$$

where γ_e is the gyromagnetic ratio for the electron.

(b) Rapid exchange. With increase of the exchange frequency, the lines are displaced towards the centre of the spectrum and merge into a single exchange-narrowed line (Fig. 3*d*), whereupon the frequency of chemical exchange becomes much greater than the frequency difference $(\omega_A-\omega_B)$, i.e. $\frac{1}{2}\tau \gg (\omega_A-\omega_B)$. For very rapid interconversions, the line broadening is given by the following expression[10]:

$$\Delta(1/T_2)=(\omega_A-\omega_B)^2\tau/4=\gamma_e(H_A-H_B)^2\tau/4, \tag{4}$$

where H_A and H_B are the resonance values of the magnetic field for forms A and B. When the rate of interconversion of forms A and B reaches the upper limit, the central line is again narrowed to its intrinsic width $1/T_{2,0}$ (Fig. 3*e*).

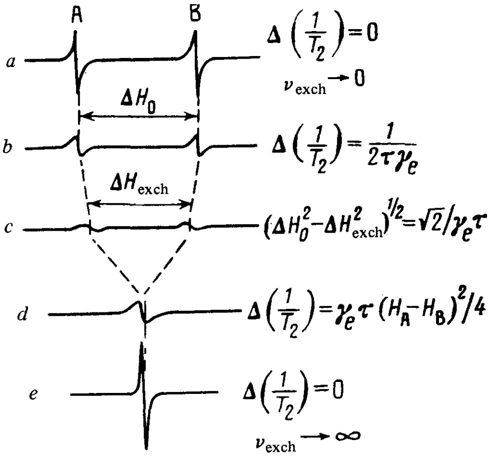


Figure 3. Schematic illustration of the influence of the rate of interconversion of the A- and B-forms of the radical on the EPR spectrum.

If the probabilities of the formation of each form of the radical involved in the exchange are P_A and P_B, the lines are displaced towards a weighted-mean position:

$$\langle H\rangle=(P_AH_A+P_BH_B)/(P_A+P_B). \tag{5}$$

This situation is reflected in Figs. 3*c* and 3*d*. The line broadening is in this case expressed by the relation[10]

$$\Delta(1/T_2)=\gamma_e\tau P_AP_B(H_A-H_B)^2. \tag{6}$$

(c) Intermediate exchange. Fig. 3 shows that, with increase of the frequency of the exchange, the lines are displaced towards the centre of the spectrum and become broadened. This shift is unambiguously related to the lifetime of the forms involved in the exchange by the following expression[10]:

$$(\Delta H_0^2-\Delta H_{exch}^2)^{1/2}=\sqrt{2}/\gamma_e\tau, \tag{7}$$

where ΔH_0 and ΔH_{exch} are the distances between the lines in the absence and presence of exchange respectively.

The two lines begin to merge into a single line when the exchange frequency is close to the frequency difference $(\omega_A-\omega_B)$. For this reason, the order of magnitude of the exchange frequency may be estimated also from the instant when the two lines merge. The relation

$$1/2\tau=(\omega_A-\omega_B)/4\sqrt{2} \tag{8}$$

corresponds to this so called intermediate exchange condition. If the frequency units are replaced by magnetic field units in oersteds, it is easy to show that

$$\nu_{\text{exch}} = 1/2\tau = 6.25 \cdot 10^{-8}(H_A - H_B). \qquad (9)$$

Thus the theory establishes an unambiguous relation between the experimental parameters of the spectrum (the widths and distance between the lines) and the kinetic parameters of the system investigated (ν_{exch} or τ).

The above relations were obtained for the simplest model where two identical EPR lines with the resonance values of the magnetic field H_A and H_B correspond to the two forms of the radical (A and B). However, in practice cases are more frequently encountered where chemical exchange entails exchange between definite HFS components within the complex EPR spectrum. The simplest instance of such exchange was examined qualitatively above in relation to the vinyl radical. The quantitative relation between the exchange frequency and the broadening of the HFS components involved in the exchange in the region of rapid and slow chemical exchange is given by the following expressions[10]:

$$\nu_{\text{exch}} = \frac{\gamma_e (\Delta a)^2 (\Delta M_I)^2}{8\Delta (1/T_2)} \text{ (rapid exchange)}, \qquad (10)$$

where Δa is the difference between the HFS constants for the forms involved in the exchange and ΔM_I the difference between the projections of the linear spins;

$$\nu_{\text{exch}} = \Delta (1/T_2)\, \gamma_e \text{ (slow exchange)}. \qquad (11)$$

If the probabilities of the formation of A and B are different and equal to P_A and P_B respectively, then Eqn. (10) is transformed into

$$(\nu_1 + \nu_{-1}) = \frac{\gamma_e P_A P_B (\Delta a)^2 (\Delta M_I)^2}{\Delta (1/T_2)}, \qquad (12)$$

where ν_1 and ν_{-1} are the rates of the forward and reverse reactions.

In practice the broadening of the HFS lines due to exchange is estimated from the amplitude of the lines, which is inversely proportional to the square of the width and is thus extremely sensitive to changes in the exchange frequency.

III. DYNAMIC EFFECTS OF THE REDISTRIBUTION OF THE UNPAIRED ELECTRON DENSITY IN RADICAL-ANIONS (CATIONOTROPISM)

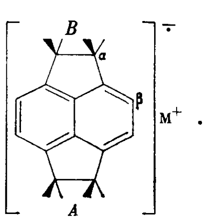
The phenomenon of the dynamic redistribution (depending on the external conditions) of the unpaired electron density between chemically equivalent parts of the molecule is frequently observed in bifunctional radical-anions. The main cause of such redistribution is cationotropism—the transfer of the cation from one functional group to another. In most organic solvents the radical-anions form ion pairs which are weakly dissociated into the free ionic species. In bifunctional radical-anions the cation is located in the vicinity of one of the two functional groups and the symmetrical distribution of unpaired electron density characteristic of the free radical-ion is thus disturbed.

The rate of cationotropic migration determines the form of the EPR spectrum to the extent that it corresponds to the conditions of rapid or slow exchange. The rate of cationotropic migration is determined in its turn by several factors: the chemical nature of the anion and cation, the solvating capacity of the solvent, and temperature.

In the study of a specific radical-anion it is usually possible to alter, within certain limits, the influence of these factors on the rate of the process and to observe how this is manifested in the EPR spectra.

Studies of this kind made it possible to put forward definite hypotheses concerning the mechanism of the dynamic delocalisation of the unpaired electron in bifunctional radical-anions. The term dynamic delocalisation is adopted to emphasise the molecular nature of the motions leading to the redistribution of the unpaired electron density between functional groups. Dynamic delocalisation is in a certain sense equivalent to a chemical reaction the only result of which is the transfer of the cation and electron density between functional groups. Analysis of the specific broadening of EPR lines makes it possible to obtain the kinetic characteristics of chemical reactions of this type.

The dynamic manifestations of cationotropism in the EPR spectra of radical-anions were observed for the first time by de Boer and Mackor[11] in relation to pyracene:



Using various solvents 1,2-dimethoxyethane (DME), tetrahydrofuran (THF), and 2-methyltetrahydrofuran (2-MeTHF), metals (Li, Na, and K), and temperatures, de Boer and Mackor found that the form of the spectra, the line widths, and the constants for the hyperfine interaction with the metal cations depend markedly on the conditions used in the observations. In DME, the solvating properties of which are more pronounced than those of THF and 2-MeTHF, spectra characteristic of the "free" pyracene radical-anion with a symmetrical distribution of the unpaired electron density relative to the symmetry axes of the molecule were observed for all the cations employed. Indeed the structure of the ion pair in DME appears to be that of a solvent-separated ion pair. In 2-MeTHF a strong interionic interaction is observed, being manifested by a breakdown of the symmetry of the spin density distribution. The constants for the hyperfine interaction of the unpaired electron with the protons of the CH_2 groups and aromatic β-protons localised in the vicinity of position A differed somewhat from the constants for the protons in the vicinity of position B. When sodium was used as the reducing agent in 2-MeTHF, hyperfine interaction with the sodium nucleus was observed in addition to the proton hyperfine structure, which indicates unambiguously the formation of a contact ion pair. When potassium was used in THF, a pattern involving the alternation of line widths was observed, which was attributed to the migration of the cation between positions A and B in the pyracene molecule. In this case there was splitting due to the interaction with the potassium nucleus, which made it possible to assign the above phenomenon unambiguously to the migration of the cation within the ion pair and to rule out intermolecular interactions.

The data discussed in this section have been classified in accordance with the nature of the functional groups.

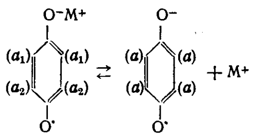
1. Semiquinones

The phenomena of ion association and cationotropism have been widely investigated in relation to semiquinone radical-anions. The use of ethereal solvents and alkali metals as reducing agents made it possible to follow and investigate quantitatively the kinetics of cationotropic migration.

Lucken[12] observed that the lithium salt of *p*-benzosemiquinone in anhydrous t-butyl alcohol gives rise to an EPR spectrum which in no way resembles that obtained previously[13]. Instead of five lines with binomial intensity ratios, Lucken recorded a spectrum comprising nine lines with the intensity ratios 1 : 2 : 2 : 1 : 4 : 1 : 2 : 2 : 1. This implies that the protons in the *p*-benzosemiquinone radical-anion have become non-equivalent in pairs; the relations between the HFS constants are as follows:

$$a_1 \neq a_2 \text{ and } a_1 \neq a,\ (a_1+a_2)/2 = a.$$

The breakdown of symmetry in the distribution of the unpaired electron density is associated with the formation of ion pairs in which the cation is linked to one of the oxygen atoms:



It has been observed[14] that, depending on the conditions, apart from the nine- and five-line spectra, other spectra are also recorded and can be used to follow the smooth transition between the extreme states of the ions; the alternation effects are clearly manifested in these intermediate spectra. Initially there were two views concerning the nature of the phenomena responsible for the alternation of line widths in the spectrum of the *p*-benzosemiquinone radical-anion. Khakhar et al.[15] believed that the alternation is associated with the equilibrium between ion pairs separated by solvent molecules and contact ion pairs and not with the dynamics of the migration of the cation. They attributed the observed alternation pattern to a superposition of the spectra of different ion pairs. Careful analysis of the line form showed subsequently[16] that the observed line width alternation pattern is in fact due to the migrations of the cations between oxygen atoms.

Oakes and Symons[17] investigated the influence of the solvent, the cation, and temperature on the EPR spectra of *p*-benzosemiquinone, durosemiquinone, and different 2,6-disubstituted semiquinones. The solvents employed were t-pentyl alcohol, t-butyl alcohol, DME, and THF, and the counterions were H^+ (hydroxy-radical), Li^+, Na^+, K^+, Rb^+, Cs^+, and $(n\text{-}Bu)_4N^+$. No migration of hydrogen between the oxygen atoms was observed for the hydroxy-radicals derived from *p*-benzosemiquinone and durosemiquinone, and in all the solvents a static pattern was found. In alcohols the lithium cation associated with *p*-benzosemiquinone and durosemiquinone radical-anions migrates at a rate corresponding to slow exchange (the lifetime of the cation near one of the oxygen atoms is $\tau = 5 \times 10^{-7}$ s). The rates of migration of the Li^+ cation in DME and THF correspond to a static pattern ($\tau = 10^{-6}$ s). In alcohols the Na^+ cation migrates at a rate corresponding to the intermediate case ($\tau = 10^{-7}$ s). Depending on the temperature, situations corresponding both to the intermediate case (+25°C) and to the static case (−60°C) are observed in ethers. The frequencies of the migration of the K^+ cation proved to be higher in all the solvents than those for Li^+ and Na^+ and, depending on the conditions, correspond to rapid, intermediate, and slow exchange processes. Oakes and Symons[17] note that the rate of migration of the cation between the oxygen atoms depends strongly on the substituents in the semiquinone:

$$2,3,5,6H \simeq 2,3,5,6\text{-Me} < 2\text{-Me} < 2,6\text{-di-Me} < 2,6\text{-di-t-Bu}.$$

The lifetimes of the cation in the vicinity of one of the oxygen atoms can be arranged in the same sequence and the migration frequencies fall in the opposite sequence. The introduction of substituents makes the oxygen atoms significantly non-equivalent, which leads to the preferential localisation of the cation in the vicinity of one of them and to a decrease of the exchange frequency.

The study of the EPR spectra at different temperatures made it possible to examine the effect of the cation and the solvent on the activation energy for the migration of the metal cation. Fig. 4 illustrates two spectra of K-*p*-benzosemiquinone[18] in DME at two temperatures; the alternation of line widths is seen at −30°C. The contributions of the cation exchange process to line width may be estimated by analysing the line intensities, and the exchange rate constants[19] and activation energies may be calculated (E = 3.4 ± 1 kcal mole^{-1}, $\lg A$ = 9.5 ± 0.5). The activation energy for cation migration varies within wide limits. Table 1 presents kinetic data for the intramolecular migration of the cation in the ion pair formed by the durosemiquinone radical-anion[20,21]. The quantity $\Delta a_H(CH_3)$ (the difference between the two observed HFI constants in the static configuration) increases with temperature, while the mean of the two HFI constants remains unchanged (1.94 ± 0.03 G). For a given series there is a linear relation between the change in the free energy of activation $\Delta G^{\neq}$ and $\Delta a_H(CH_3)$. The negative activation entropy shows that the degree of order in the activated state is greater than that in the reactants and that the activated complex is more solvated than the ion pair.

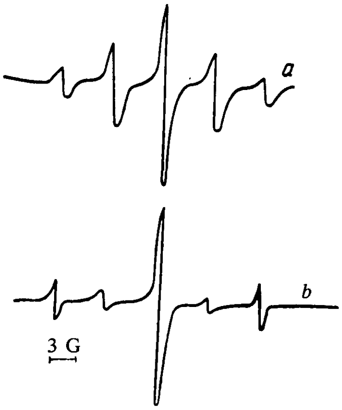
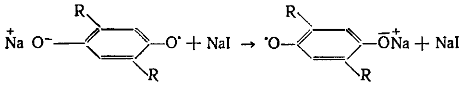


Figure 4. The EPR spectrum of the ion pair comprising the *p*-benzosemiquinone radical-anion and the potassium cation in DME different temperatures (°C): *a*) 20°; *b*) −30°C.[18]

The migration of the cation from one oxygen atom to the other in the semiquinone radical-anion may occur as a bimolecular process. Line width alternation effects in the EPR spectrum of the Na–2,5-di-t-butyl-*p*-benzosemiquinone radical-ion pair were observed[22] following the addition of NaI to a solution in THF. The authors found from the temperature dependence of the rate constant for the process



(R = t-butyl).

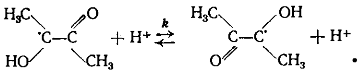
that the activation energy is 2.5 kcal mole^{-1} and the pre-exponential factor is 5.6 × 10^{10} litre mole^{-1}s^{-1}.

Table 1. The activation energies and pre-exponential factors for the cation migration in durosemiquinone radical-anions (D).

Ion pair	Solvent	E, kcal mole^{-1}	$10^{-10}A$, s^{-1}
Na-D	DME	3.57±0.20	0.12
Na-D	THF	5.61±0.23	0.47
K-D*	DME	5.27	14
K-D*	THF	7.39±0.52	470
Cs-D	DME	4.46±0.27	54
Cs-D	THF	4.82±0.28	660
Cs-D	MeTHF	3.70±0.25	6.9
K-D	DME	5.05±0.34	52
K-D	THF	6.2±0.20	270

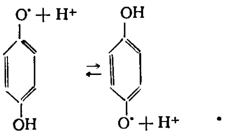
*Data from Prahananda et al.[21]

A similar mechanism has been proposed to explain the acid-catalysed proton transfer in the monoprotonated *trans*-semidione radical[23]. The authors obtained it in a water flow system at 23°C by one-electron reduction of diacetyl. At pH 0.5 they observed a spectrum consisting of a binomial septet (a_H = 8.3 G); at pH 1 appreciable line width alternation was observed in the spectrum. At pH 2 the pronounced alternation converts the septet into a 1 : 9 : 9 : 1 quartet with an HFI constant of 16.6 G. At pH 3 the two methyl groups become non-equivalent and a splitting due to the one proton of the OH group appears: $a_H(CH_3)$ = 12.8 G; $a_H(CH_3)$ = 3.8 G; $a_H(OH)$ = 2.0 G. This result was attributed to acid-catalysed proton transfer between oxygen atoms:

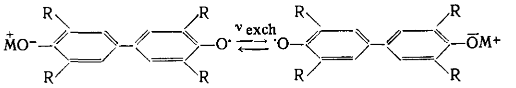


The rate constant is 4.53 × 10^9 litre mole^{-1}s^{-1}.

Smith and Carrington[24] observed a dependence of the line width on pH in the spectrum of the monoprotonated *p*-benzosemiquinone radical-anion (the 4-hydroxyphenoxy-radical), which they attributed to the process



There exists yet another factor which may influence the exchange frequency. It is the distance between the oxygen atoms, which may be altered by employing quinones of different structures. We investigated[25] the EPR spectra of the radical-anions derived from 3,3′,5,5′-tetra-t-butyldiphenylquinone (TBDP). The observed line width alternation patterns made it possible to measure the cation exchange frequencies:

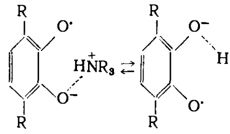


(R = t-butyl).

The order of magnitude of the values of ν_{exch} for the TBDP radical-anion corresponds to that of the cation migration frequencies in *p*-benzosemiquinones, although the cation localisation centres in the radical-anion which we investigated are separated by a much greater distance. The cause of this phenomenon is apparently the fact that the cation migration frequency is determined mainly by the depth of the energy minima on the potential curves corresponding to the limiting structures and by the distance between these minima. The minima for *p*-benzosemiquinone are fairly close. The energy minima for the "limiting" structures of TBDP are much further apart, although their depth is smaller owing to the extensive conjugation system and this leads to the same cation migration frequencies as in benzosemiquinones.

The *o*-benzosemiquinone radical-anions are systems in which the oxygen atoms are much closer to one another. The EPR spectra of 3,6-di-t-butyl-*o*-benzosemiquinone radical-anions[26] in different solvents, at different temperatures, and in the presence of different metal cations always exhibit a symmetrical unpaired electron density distribution. This implies that the cations either occupy a symmetrical position in relation to the oxygen atoms or migrate at a high frequency.

The use of alkylammonium cations in an ion pair incorporating the 3,6-di-t-butyl-*o*-semiquinone anion leads to effects associated with a dynamic redistribution of the unpaired electron density, which was attributed to the migration of the hydrogen bond between oxygen atoms[27]:

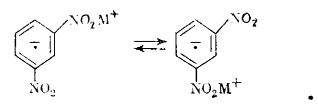


(R = t-butyl).

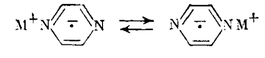
2. Cationotropism in Ion-Pairs Formed by Dinitrobenzene Radical-Anions and in Certain Other Bifunctional Radical-Anions

Line width alternation effects have been found in ion pairs formed by *o*-, *m*-, and *p*-dinitrobenzene radical-anions[28–33]. The alternation is caused by the migration of the cations between the nitro-groups. Symons and coworkers[18,19] [wrong references?] obtained the *p*-dinitrobenzene radical-anions by the photolysis of a methanol solution containing sodium methoxide. The addition of solvents promoting the formation of ion pairs caused line width alternation. In the *o*-dinitrobenzene radical-anion the sodium cation migrates at room temperature at a frequency corresponding to the rapid exchange conditions. A decrease of temperature to −60°C causes the appearance of the alternation effect. The slow exchange situation is not observed. A similar behaviour has been observed for potassium cations[33]. For caesium cations, only rapid exchange is observed at all temperatures.

Slow exchange is observed in the sodium salt of the *m*-dinitrobenzene radical-anion at all temperatures. In the potassium salt at low temperatures there is slow exchange but at 0° C alternation effects appear. In the EPR spectra of the caesium and rubidium salts a transition is observed from slow exchange at low temperatures to a distinct line width alternation pattern at room temperature:

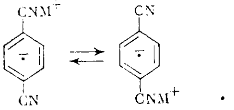


The formation of ion pairs comprising the pyrazine radical-anion and the sodium cation has been investigated[34]:



At room temperature the EPR spectrum reveals hyperfine interactions with the two nitrogen nuclei ($a_N = 7.14$ G), with the four protons ($a_H = 2.70$ G), and with the sodium nucleus ($a_{Na} = 0.55$ G). At lower temperatures alternation effects associated with the migration of the cation appear. The process activation energy is $E_a = 7.1 \pm 0.5$ kcal mole^{-1} and $A = 2 \times 10^{13}$ s^{-1}. The activation energy for the caesium cation proved to be much higher: $E_a =$ 15 kcal mole^{-1}.

Nakamura[35] investigated the exchange of the sodium cation in the terephthalonitrile radical-anion:



The activation energy in THF proved to be $E_a = 5 \pm 1$ kcal mole^{-1} for sodium and $E_a = 3.7 \pm 0.5$ kcal mole^{-1} for potassium.

3. The Radical-Anions of Bridged Compounds

Numerous studies have been devoted to the distribution of the unpaired electron density in systems having the general structure $[\text{Ar–X–Ar}]^{\bar{\cdot}}\text{M}^+$, where Ar are either aromatic radicals or π-electron functional groups and X are isolating bridges of different lengths and structures[36]. The interest in these systems is due to the hypothesis that the study of the distribution of their unpaired electron density can yield information about the ability of the X groups to "transmit" the unpaired electron from one aromatic fragment to the other. However, later studies showed that this simplified electron transfer mechanism, which depends only on the transmittivity of the –X– bridge, does not take into account the formation of ion pairs. Studies of the EPR spectra of the radical-anions $[\text{Ar–X–Ar}]^{\bar{\cdot}}\text{M}^+$ showed that the nature of the solvent and temperature have a strong influence on the distribution of the unpaired electron density and on the frequency of electron transfer between the aromatic fragments.

The hypothesis that the migration of the metal cation plays a decisive role in the dynamic delocalisation of the electron in the radical-anions of bridged compounds was not immediately demonstrated experimentally. The clearest example is provided by the study of Gerson and Martin[71], who investigated the EPR spectra of diphenylmethane and *p*-deuterodiphenylmethane in DME and showed that the unpaired electron is delocalised over the two benzene rings. It is believed[72,73] that the annular 1,3-interaction between the benzene rings determines the mechanism of the electron transfer between them. However, this idea conflicts with data which the same authors obtained in a study of the EPR spectrum of the diphenylmethane radical-anion in MeTHF.[72] A static picture, corresponding to the localisation of the unpaired electron in one benzene ring, was observed, which is inconsistent with the concept of the decisive role of annular 1,3-interactions.

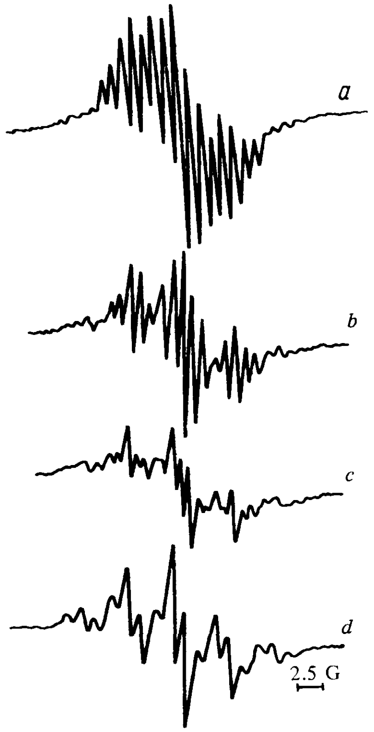
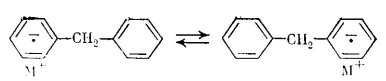


Figure 5. The EPR spectrum of the ion pair comprising the diphenylmethane radical-anion and the potassium cation in a mixture of diethyl ether and 10% of hexamethylphosphoramide at different temperatures (°C): *a*) –70; *b*) –100; *c*) –110; *d*) –127.

The authors of the present review investigated the exchange of the unpaired electron in the diphenylmethane radical-anion in various solvents and at various temperatures[37-40]. The rapid exchange condition holds in DME (K^+ cation) over the entire temperature range. In a 1 : 1 DME : THF mixture at –70° C there is also a rapid exchange. When the temperature is reduced to –100° C, alternating line width effects appear. As a result, the relatively complex EPR spectrum is converted into a spectrum in which five principal lines are distinctly visible; EPR spectra of this type usually arise from the radical-anions of alkylbenzenes[36]. Analysis of the hyperfine structure of the spectrum showed that the exchange frequency corresponds to the intermediate case in relation to the hyperfine interaction with the *ortho*- and *meta*-protons; the rapid exchange condition holds in relation to *para*-protons. The exchange frequency is $\nu_{exch} = 10^{12} \exp(-4000/RT)(s^{-1})$. The slow exchange condition was achieved[40] when ethyl ether containing 10% of hexamethylphosphoramide was used as the solvent. Fig. 5 presents the EPR spectra corresponding to the conditions of the rapid (*a*), intermediate (*b*) and (*c*) and slow (*d*) exchange processes, the exchange frequency being given by $\nu_{\text{exch}} = 2.3 \times 10^{13} \exp(-4300/RT)$.

The nature of the influence of the solvent and temperature shows convincingly that the solvating capacity of the solvent determines the mobility of the metal cation on which the fulfilment of rapid or slow exchange conditions depends. A distinctive feature of the diphenylmethane radical-anion compared with the systems discussed above is the separation of the functional groups (benzene rings) by a considerable energy barrier due to the methylene group. As a result of this feature, the unpaired electron is fully transferred from one benzene ring to the other:



In *p*-benzosemiquinone radical-anions the migration of the cation causes only a partial redistribution of electron density between oxygen and carbon atoms within the limits of the common π-electron system.

Similar effects of temperature and the solvent were observed for other radical-anions—those of $\alpha\alpha'$-dinaphthylmethane and 1,2-di(α-naphthyl)ethane[37]. A similar situation has been observed in a study of exchange via the $>\mathrm{Si}(C_2H_5)_2$ group in the radical-anion $Ph_2Si(C_2H_5)_2^{\overline{\cdot}}K^+$ in THF:[41] $\nu_{\text{exch}} = 10^9 \exp(-2800/RT)$ (s^{-1}).

Apart from the "two-well" systems discussed above, more complex systems have been investigated—"three-well" (triphenylmethane radical-anions)[42] and "four-well" systems (tetraphenylsilane radical-anions)[41]. Fig. 6 presents the EPR spectrum of the tetraphenylsilane radical-anion in THF (K^+ cation). The spectrum at −40°C (*a*) consists of the principal quintet arising due to four *para*-protons (a_p = 2.2 G). Each line of the quintet is split into nine lines due to the eight *ortho*-protons (a_0 = 0.8 G). At −140°C the spectrum is converted into a poorly resolved doublet with a splitting of 8 G, which indicates the localisation of the unpaired electron in one benzene ring only.

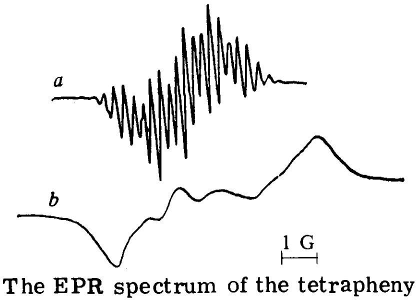


Figure 6. The EPR spectrum of the tetraphenylsilane radical-anion in THF at different temperatures (°C): *a*) −40; *b*) −140.

The systems considered hitherto have equivalent cation localisation centres. In the *p*-dibenzylbenzene radical-anion the two extreme benzene rings are structurally different from the central ring and the probability of finding the metal cation near the centre of the molecule should be different from the probability of finding the cation at its edges[43]. This should be the case primarily in the region of slow exchange, where the spectrum corresponds to the localisation of the cation near one of the benzene rings:

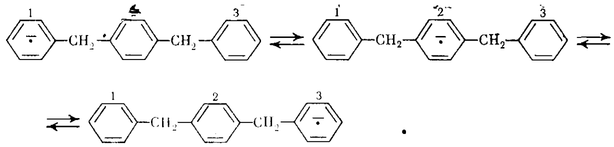


Fig. 7 illustrates one of the spectra recorded in THF, DME, and their mixtures (potassium cation) at −60° and −70°C. A decrease of temperature and the addition of ethyl ether cause a transformation of this fairly complex spectrum into a quintet characteristic of *p*-dialkylbenzenes. Analysis of the spectrum shows that at a low temperature the cation is localised near the central benzene ring. The principal quintet splitting of 4.67 G is due to the interaction with the four protons of the central benzene ring and the additional splitting (1.14 G) is due to the interaction with the four protons of the two methylene groups. Analysis of the line width alternation effects showed that the potassium cation migration frequency at −60° and −70°C between benzene rings *1*, *2*, and *3* and the corresponding unpaired electron delocalisation frequency are within the following limits (s^{-1}): $10^7 > \nu^{1-3} > 3 \times 10^6\ s^{-1}$; $\nu^{1-2} = \nu^{2-3} > 10^7\ s^{-1}$. At −100°C the exchange frequency is $\nu^{1-2} = \nu^{2-3} > 10^7\ s^{-1}$.

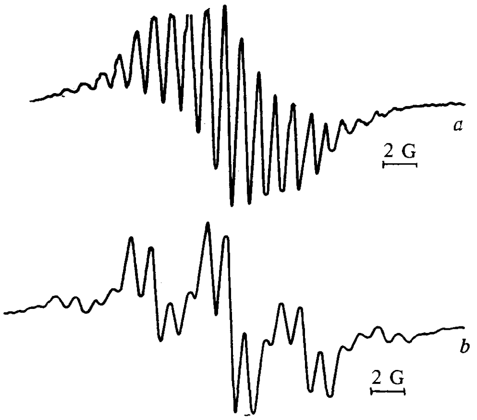


Figure 7. The EPR spectrum of the ion pair comprising the *p*-dibenzylbenzene radical-anion and the potassium cation in THF, DME, and their mixture at −60° and −70°C (*a*) and in a mixture of 90% of diethyl ether and 5% of hexamethylphosphoramide at −100°C (*b*).

Non-aromatic bridged systems have also been investigated. Syrkin et al.[44] found that in the electrochemical generation of difluorodinitromethane anions there is rapid electron exchange between the nitro-groups. On the other hand, a static picture involving the localisation of the unpaired electron in one of the nitrated aromatic components of the molecule is observed in the di-$\alpha\alpha$-difluoro-di-(4-nitrophenyl)methane[45]. A static picture is also characteristic of the dibenzyl[46] and di-(4-nitrophenyl)methane radical-anions[47].

4. The Mechanism of the Dynamic Delocalisation of Electrons in Bifunctional Radical-Anions

Before considering the mechanism of the dynamic delocalisation of the electron (cationotropism), it is necessary to examine the causes responsible for the asymmetric disposition of the cation in the ion pairs formed by bifunctional radical-anions. If the exchange interaction is fully disregarded, then the nature of the bond between the anion and the cation in the ion pair reduces exclusively to electrostatic forces. A simple calculation shows that the Coulombic interaction energy between the cation and anion increases if the cation is located near one of the functional groups, to which an excess (compared with the free ion) negative change density is drawn under the influence of the electric field of the cation. Thus an asymmetric structure of the ion pair formed by a radical-anion having two functional groups is energetically more favourable than the symmetrical disposition of the cation. An asymmetric distribution of the unpaired electron density leads to some loss of exchange energy but in the case of bridged compounds the latter is apparently small; in other cases the loss may be appreciable. It appears that for this reason it is impossible to ensure the location of the unpaired electron in a single benzene ring of the biphenyl radical-anion by selecting appropriate conditions. It is quite likely that in this case the loss of exchange energy owing to the separation of the π-electron systems of the benzene rings is not compensated by the gain in Coulombic energy. The degree of redistribution of the unpaired electron density in a particular radical-anion as a function of the nature of the cation and the solvent is a qualitative measure of the bond strength in the ion pair.

Several models have now been proposed for the description of the dynamic delocalisation of the unpaired electron. McConnell[48] considered the delocalisation of the unpaired electron in the radical-anions of $\alpha\omega$-diphenylalkanes. The interaction with the medium was taken into account with the aid of the formal effect involving the self-localisation of the charge without taking into account the structure of the ion pairs. McConnell analysed the ability of $(-CH_2-)_n$ bridges of different lengths to transmit an electron.

Claxton[49] considered the exchange of the cation between the nitrogen atoms of the pyrazine radical-anion and postulated the liberation of the cation from the solvent cage containing the radical-anion. After the cation leaves the cage, the radical-anion rotates in the latter independently of the cation. This rotation ensures the migration of the cation when it re-enters the solvent cage. By studying the reaction coordinate, Claxton found that the cation moves from one atom to another, deviating from the plane of symmetry of the molecule.

It is noteworthy that both models considered do not take into account the specific structure of ion pairs. Presumably the mechanisms of the dynamic delocalisation of the unpaired electron in bifunctional aromatic radical-anions and in bridged compounds have common features. These features are associated with the decisive role of the mobility of the cation. The difference between them is that in bifunctional aromatic radical-anions there are no energy barriers preventing the delocalisation of the electron, since the positions of the cations are linked by the common π-electron system. At the present time the mechanism of the dynamic delocalisation cannot be treated in isolation from modern ideas concerning the structure of ion pairs. We believe that the dynamics of the migration of the cation is indissolubly linked to the interconversions between contact ion pairs and ion pairs separated by solvent molecule.

Evidently the Coulombic interaction between the radical-anion and the cation in a solvent-separated ion pair is much weaker than the interaction in a contact ion pair. The cation in a solvent-separated ion pair is less able to distort the distribution of the unpaired electron over the radical anion. Thus for the interconversions of ion pairs having different structures to play a significant role in the dynamic delocalisation mechanism, they must take place with frequencies of approximately 10^7–10^8 s^{-1}. Such frequencies are indeed observed in the reactions of ion pairs[50]. There is a complete parallelism between the influences of the nature of the cation and the solvent on the rate of dynamic electron delocalisation and on the interconversions of ion pairs. In solvents such as THF and diethyl ether (DEE), where the formation of contact ion pairs takes place more readily than in DME, dynamic delocalisation processes are much slower than in DME. Analysis of experimental data showed that the activation energy for the migration of the cation is determined by the nature of the ion pair.

Presumably the conversion of a contact ion pair into a solvent-separated one is the initial stage in the cation migration processes. Furthermore, it is necessary that during the lifetime of the solvent-separated ion pair there is sufficient time for the cation to pass to a new location in the radical-anion. The influence of the solvent and the cation on processes associated with the dynamic delocalisation of the unpaired electron in a specific radical-anion reduces mainly to a change of bond strength in the ion pair. On the other hand, in considering different radical-anions, one must take into account the geometrical factors in the locations of the cation. A large distance between them or an unfavourable conformational disposition may increase the time taken for the transfer of the cation to such an extent (static case) that the application of the EPR method to the estimation of the kinetic parameters of the cationotropic migration becomes ineffective.

In the majority of the bifunctional aromatic radical-anions considered above, the functional groups are fairly close and the rate-limiting stage is apparently merely the dissociation of the bond in the ion pair. In the radical-anions derived from bridge compounds, increase of the distance between the locations of the cation leads to a decrease of the delocalisation frequency owing to the longer migration of the cation[39,51].

An unambiguous answer to the question of the ability of bridge groups to transmit an electron cannot be obtained from EPR data, because the delocalisation frequency depends on the mobility of the cation. One can only assume that, in the presence of a small number of units in the bridge group, an exchange interaction (with an intensity corresponding to approximately 10^{-5}–10^{-7} eV), which is necessary to ensure the "intrinsic" exchange frequencies in the "free" radical-anion (approximately 10^9–10^7 s^{-1}), takes place.

The phenomenological picture considered above reflects only the most general features of the exchange processes. In a quantitative treatment of the experimental data for the rates of exchange or the constants for equilibria involving ion pairs of radical anions one frequently encounters additional effects associated with the dependence of the properties of the solvent on temperature[25,52]. Over a wide temperature range, the dielectric constants of solvents vary within broad limits, which leads to appreciable additional shifts in the equilibria between ion pairs having different structures. Change in the properties of the solvent frequently leads to appreciable deviations from the Arrhenius relation for the rate and equilibrium constants. For this reason, all the activation energies and rate constants for exchange processes as a rule refer to narrow temperature ranges.

IV. DYNAMIC DELOCALISATION OF THE UNPAIRED ELECTRON IN FREE RADICALS

The examples considered in the previous section, which illustrate the cationotropisms in ion pairs formed by radical-anions, constitute the type of tautomerism of radicals which has been investigated in greatest detail and which differs from the classical tautomerism by the migration of ionic and not covalent bonds. The tautomerism of radicals, accompanied by the migration of organic or organoelemental fragments between equivalent positions in radicals and the synchronous redistribution of the unpaired electron density in such species, is considered below.

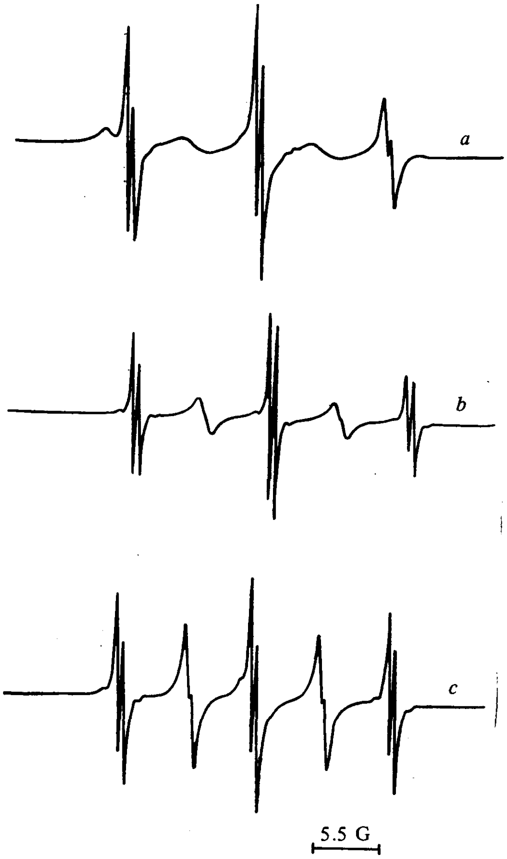
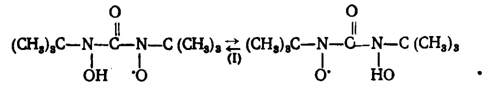


Figure 8. The EPR spectra of radical (I) at different temperatures (°C): *a*) −80; *b*) 0; *c*) 60.

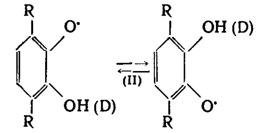
1. Migration of Hydrogen and Deuterium

The simplest examples of this type of tautomerism are the intramolecular migration of hydrogen and deuterium atoms. Analysis of the line width in the EPR spectra[53] demonstrated the possibility of the migration of the hydrogen atom in radical (I) having the following structure:



$$(CH_3)_3C-\underset{OH}{N}-\overset{O}{\overset{\|}{C}}-\underset{\cdot O}{N}-C(CH_3)_3 \underset{(I)}{\rightleftarrows} (CH_3)_3C-\underset{O\cdot}{N}-\overset{O}{\overset{\|}{C}}-\underset{HO}{N}-C(CH_3)_3$$

At low temperatures (−90° C) the EPR spectrum of this radical is a triplet due to the interaction of the unpaired electron with the nitrogen nucleus (a_N = 10.4 G), each component of which is split into a doublet by the proton of the hydroxy-group [a_H(OH) = 0.5 G] (Fig. 8). With increase of temperature, the spectrum is transformed into a quintet (owing to the two equivalent nitrogen atoms) with an HFI constant smaller by a factor of two than the constant due to one nitrogen atom. The energy barrier to the migration of hydrogen is 2.7 ± 0.3 kcal mole^{-1}. The authors of the present review demonstrated almost simultaneously[54,55] the occurrence of the intramolecular migration of hydrogen and deuterium atoms in the 3,6-di-t-butyl-2-hydroxyphenoxy-radical (II):



(R = t-butyl).

Fig. 9*a* illustrates the EPR spectrum of this radical at 60° C.

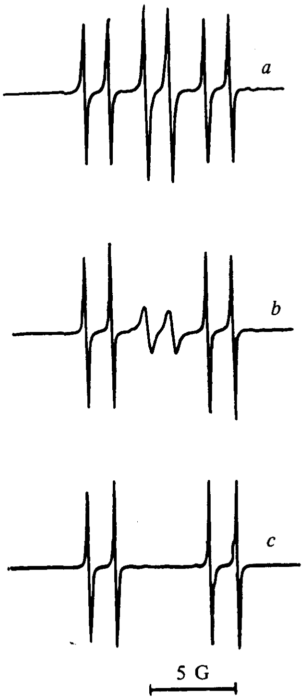


Figure 9. The EPR spectra of radical (II) in toluene at different temperatures (°C): *a*) 60; *b*) 0; *c*) −60.

The triplet (a_H = 3.92 G) is due to the interaction of the unpaired electron with the "equivalent" ring protons; each component of the triplet is split into a doublet by the proton of the hydroxy-group [a_H(OH) = 1.6 G]. In the spectrum of the analogue of radical (II) deuterated at the hydroxy-group each component of the triplet consists of three lines owing to the interaction of the unpaired electron with the deuterium nucleus [a_D(OD) = 0.26 G] (Fig. 10*a*). With increase of temperature, the central component of the triplet is broadened (the breakdown of the "equivalence" of the ring protons), indicating the inhibition of the intramolecular migration of hydrogen (deuterium) atoms between the oxygen atoms in radical (II).

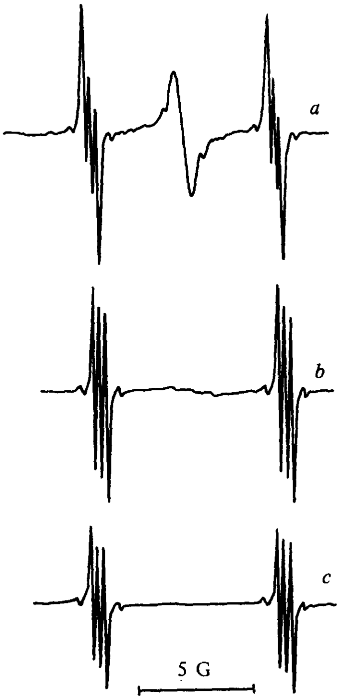
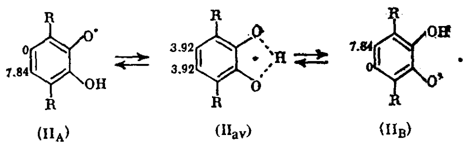


Figure 10. The spectra of radical (II), deuterated in the hydroxy-group, in toluene at different temperatures (°C): *a*) 60; *b*) 0; *c*) −60.

At fairly low temperatures (below −60°C) migration ceases on the EPR time scale (~ 10^{-7} s) and a spectrum corresponding to one of the "frozen" structures (II_A) or (II_B) is observed (Figs. 10*c* and 11*c*). The HFI constants for structures (II_A) and (II_B) (slow exchange) as well as (II_{av}) (rapid exchange) are given below for greater clarity:



(R = t-butyl).

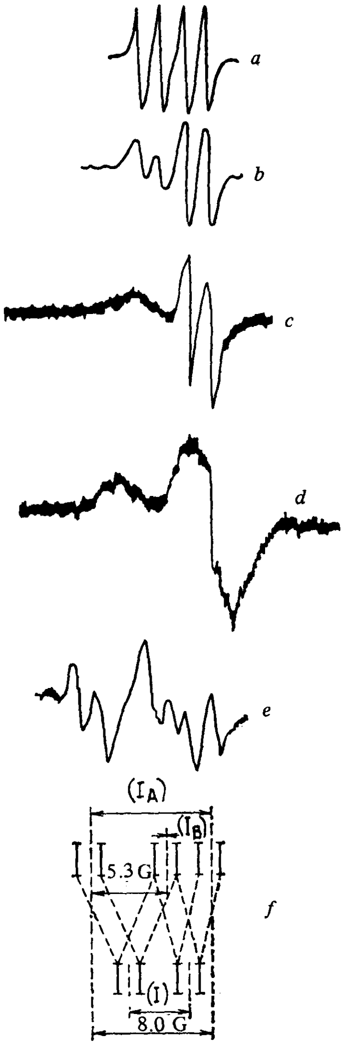


Figure 11. The EPR spectra of radical (V) in diethyl ether at different temperatures (°C): *a*) 100; *b*) 20; *c*) 0; *d*) −20; *e*) −100; *f*) schematic representation of the spectra of radical (V) under slow exchange conditions.

Analysis of the line widths made it possible to determine the kinetic parameters of the migration of hydrogen and deuterium atoms and to estimate the kinetic isotope effect. The frequencies of the intramolecular migration of hydrogen (ν_H) and deuterium (ν_D) atoms in radical (II) are listed below (solvent—heptane):

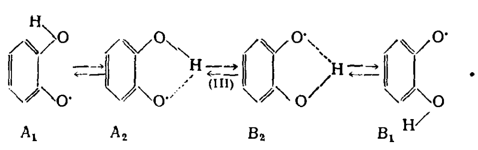
t, °C	$10^{-9}\nu_H$, s^{-1}	$10^{-9}\nu_D$, s^{-1}	ν_D/ν_H (expt.)	ν_D/ν_H (calc.)
20	3.2	0.3	0.08	0.09
60	5.5	0.75	0.14	0.12
80	6.3	1.0	0.16	0.14
120	10.0	2.2	0.22	0.17

Activation energies of 2.9 and 4.5 kcal $mole^{-1}$ respectively were determined from the temperature dependence of ν_H and ν_D. The experimental isotope effect agrees well with the value calculated theoretically from the following expression:

$$\frac{\nu_D}{\nu_H} = \exp\left\{\frac{hc}{2kT}(\tilde{\nu}_{OD} - \tilde{\nu}_{OH})\right\}, \qquad (13)$$

where $\tilde{\nu}_{OD}$ and $\tilde{\nu}_{OH}$ are the stretching vibration frequencies of the OD and OH bonds determined from the infrared spectra of sterically hindered phenols. It has been shown[56] that solvents capable of forming hydrogen bonds inhibit the migration of hydrogen in radical (II). The complete set of results obtained made it possible to conclude that the migration of hydrogen atoms has a homolytic mechanism and is in essence an intramolecular radical substitution reaction.

Later Loth et al.[57] observed an analogous effect in the unsubstituted 2-hydroxy-phenoxy-radical (III), the EPR spectra of which exhibit a specific broadening of the lines—a hyperfine structure. However, analysis of the spectra is complicated in this instance by the hindered rotation of the OH bond and the occurrence of the conformers A_1, A_2, or B_1, B_2, which differ in their structures and thermodynamic stabilities:



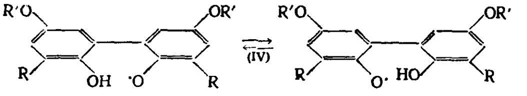
The hydrogen migration frequencies (ν_H) and deuterium (ν_D) in radical (III)[57] are listed below:

t, °C	$10^{-5}\nu_H$, s^{-1}	t, °C	$10^{-5}\nu_D$, s^{-1}
22	191	72	21.4
5	96.1	58	14.8
−25	16.0	38	5.12
−55	1.62	18	1.78

The activation energies are 8.2 ± 0.1 and 9.5 ± 0.5 kcal $mole^{-1}$ respectively. Owing to the possibility of the existence of the above conformers, the migration frequencies of hydrogen and deuterium in radical (III) are much lower than those in radical (II), where the presence of the bulky t-butyl groups prevents the rotation of the OH group, and the radical exists in a form where the hydrogen atom is virtually in the plane of the aromatic ring (of type A_2 or B_2). The sharply reduced migration frequencies in radical (III) may be due to the fact that the rate-limiting stage in the intramolecular transfer is not the dissociation of the OH or OD bonds, but the stage defined by the lifetime of the conformers A_2 or B_2, simulating the transition state in the transfer of hydrogen and deuterium. Analysis of the planar conformers (A_2, B_2) showed that the difference between the O–H and O...H bond lengths is small and amounts to only 0.3 Å.

The authors explain the anomalous kinetic isotope effect (approximately 100) for radical (III) by the fact that, apart from the stretching vibrations of the OH and OD bonds, account must be taken of the contributions of all the vibrations characteristic of the COOH fragment.

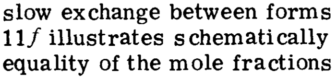
The EPR spectra of radicals (IV),



(R = t-butyl).

were observed quite recently[58]. The HFI constants of the ring protons and α-hydrogen atoms of the alkoxy-substituents are equivalent in pairs and in the temperature range from −50° to 25°C there is no alternation of line widths. This led the authors to the conclusion that rapid intramolecular processes take place in radicals of this type. It is noteworthy that the HFI constants for the ring protons ($a_H^{3,3'} = 1.4$ G) and the protons in the alkoxy-substituents [$a_H(OCH_3) = 0.83$ G] are small and that in this case the rapid exchange condition may be fulfilled for the usual exchange frequencies (~ 10^7–10^8 s^{-1}).

The examples discussed above illustrate the simplest instances of degenerate tautomerism—the migration of hydrogen and deuterium atoms between equivalent positions in the radical. The intramolecular migration of hydrogen and deuterium atoms in the 3,5-di-t-butyl-2-chloro-6-hydroxyphenoxy-radical (V), which constitutes the simplest example of non-degenerate tautomerism:



(V_A) (V_B)

(R = t-butyl).

has been investigated[59]. In diethyl ether at low temperatures the EPR spectrum of radical (V) is a doublet (a_H = 3.3 G) due to the interaction of the unpaired electron with a ring proton; each component of the doublet contains two lines (a_H = 1.5 G) owing to the hydroxyl proton (Fig. 11*a*). With decrease of temperature, the downfield component of the ring proton doublet is broadened, virtually disappearing at 0°C (Figs. 11*b* and 11*c*). On further decrease of temperature, the hydroxyl doublet coalesces (Fig. 11*d*) and at −100°C the observed spectrum consists of a superposition of two signals with slightly different *g* factors (Fig. 11*e*): a doublet with a_H = 8.0 G, each component of which is split in two (a_H = 1.5 G), and a second doublet a_H = 1.5 G.

The above changes in the spectra are fully reversible when the temperature is altered and indicate the occurrence of dynamic effects due to the intramolecular migration of a hydrogen atom between oxygen atoms. At higher and lower temperatures respectively the conditions for rapid and slow exchange between forms (V_A) and (V_B) obtain. Fig. 11*f* illustrates schematically these two instances for equality of the mole fractions of forms (V_A) and (V_B). This interpretation of the EPR spectra is confirmed by the comparative analysis of the spectrum of the deuterated analogue of radical (V). The doublet with a_H = 8.0 G refers to the (V_B) form, while the spectrum without HFI due to the ring proton refers to the (V_A) form. Analysis of the temperature dependence of the HFI of the ring proton in the high-temperature spectra (rapid exchange) made it possible to estimate the constant for the equilibrium between forms (V_A) and (V_B), from the expression

$$K_p = \frac{\alpha}{1-\alpha} = \frac{\tilde{a}}{a_{V_A} - \tilde{a}}, \qquad (14)$$

where $\tilde{a} = \alpha a_{V_A} + (1 - \alpha) a_{V_B}$, α is the mole fraction of form (V_A), and a_{V_A} = 8.0 G and a_{V_B} = 0 G are respectively the HFI constants for the ring proton in the corresponding forms. The thermodynamic parameters obtained in this way are $K_p(20°) = 0.83$ and $\Delta H = -0.33$ kcal $mole^{-1}$ (toluene). The greater thermodynamic stability of form (V_A) follows from the fact that the electrons in the outer shell of the chlorine atom, located in this form in the *ortho*-position relative to the univalent oxygen atom, interact more effectively with the unpaired electron of radical (V), increasing its stabilisation energy.

The thermodynamic data obtained and analysis of the broadening in the EPR spectra made it possible to obtain the rate constants (k_1 and k_{-1}) for the reversible proton transfer between forms (V_A) and (V_B). The hydrogen and deuterium migration frequencies for radical (V) in toluene are listed below:

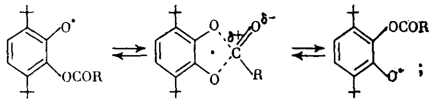
t, °C	$10^{-8}k_1(H)$, s^{-1}	$10^{-7}k_1(D)$, s^{-1}	$k_1(D)/k_1(H)$ (expt.)	$k_1(D)/k_1(H)$ (calc.)
20	4.1	3.0	0.07	0.09
40	6.5	5.6	0.09	0.11
60	9.5	9.6	0.10	0.12
80	19	25.0	0.13	0.14

The activation energies are respectively 4.1 ± 0.5 and 5.7 ± 0.5 kcal mole^{-1}. As for radical (II), the kinetic isotope effect is described satisfactorily by Eqn. (13). In solvents capable of forming hydrogen bonds (for example in diethyl ether) the constants K_p hardly change, but the rate constants k_1 and k_{-1} decrease appreciably, which makes it possible to observe the spectra of the individual species at low temperatures corresponding to the slow exchange conditions.

2. Migration of Fragments with Group IV Elements

In the search for further examples of the tautomerism of radicals, the authors of the present review turned to radicals containing substituents with Group IV elements (carbon and tin). The migration of the methyl group between oxygen atoms in the 3,6-di-t-butyl-2-methoxyphenoxy-radical (VI)† was not observed up to 200°C. The hyperfine structure of the EPR spectrum of this radical does not exhibit a specific broadening of the lines over the entire temperature range; the spectrum consists of a doublet of doublets due to the interaction of the unpaired electron with the *para*-proton (a_H = 8.65 G) and the *ortho*-protons (a_H = 1.0 G) of the aromatic ring; each component being a quartet owing to the protons of the methyl group [$a_H(CH_3)$ = 1.37 G].

The intramolecular migration of carbon-containing groups with EPR frequencies has been observed for acylotropic migration in 2-acyloxy-3,6-di-t-butylphenoxy-radicals[60,61]:



R = $COCH_3$ (VII), COC_2H_5 (VIII), $COCH_2Br$ (IX), $COCH_2C_6H_5$ (X), or $COCH(C_6H_5)_2$ (XI) .

The EPR spectrum of radical (VII) is illustrated in Fig. 12. The doublet with a_H = 10.2 G is due to the interaction of the unpaired electron with the ring proton in the *para*-position relative to the "univalent" oxygen atom. Each component of this doublet is split into two lines due to the *meta*-proton of the aromatic ring (a_H = 1.95 G). The above interpretation of the spectrum is fully consistent with the unpaired electron density distribution characteristic of phenoxy-radicals: an appreciable positive spin density is observed in the *para*-position of the phenoxy-ring and the HFI constant is between −8 and 10 G, while in the *meta*-position the spin density is negative and the HFI constant is between 0.5 and 2.2 G. The EPR spectra of radicals (VIII)–(XI) are analogous to the spectrum of radical (VII).

With increase of temperature (to 120°C) a distinct broadening of the extreme HFS component is observed in the EPR spectra of radicals (VII)–(X) (Fig. 13) due to the migration of the acyl group between the oxygen atoms. It is noteworthy that the broadened lines are not displaced, i.e. the slow exchange condition is fulfilled. Under the rapid exchange condition, which does not obtain in the given experiment, the EPR spectra of radicals (VII)–(X) should consist of a triplet, due to the "equivalent" ring protons, with an HFI constant of (10.2−1.95)/2 = 4.1 G. In the case under consideration, corresponding to slow exchange, the spectral lines with overall nuclear spin projections $M_I(+1/2, +1/2)$ and $M_I(-1/2, -1/2)$ hardly change their positions, while the lines with $M_I(+1/2, -1/2)$ and $M_I(-1/2, +1/2)$, should be converted into the line with $M_I(0)$ in the spectrum corresponding to rapid exchange. The opposite signs of the nuclear spin projections of the aromatic ring protons are due to the opposite signs of the spin intensities at the corresponding carbon atoms, which leads to the broadening of the extreme HFS components[60].

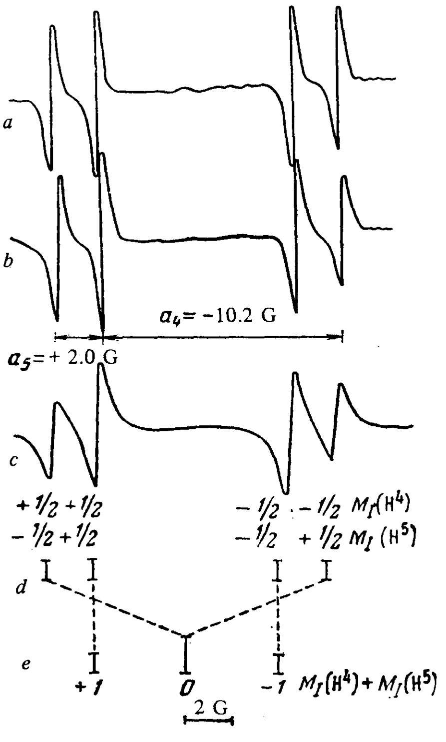


Figure 12. The EPR spectra of radical (VII) in benzene at different temperatures (°C): *a*) 80; *b*) 100; *c*) 120; *d*) and *e*) schematic representation of the spectra under the conditions of slow and fast exchange respectively.

The kinetic parameters of the acylotropic migration in radicals (VII)–(XI) were calculated on the basis of the analysis of the line width[61]. The influence of the substituent on the kinetic parameters of the acylotropic migration

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† A.I. Prokof'ev, T.I. Prokof'eva, N.N. Bubnov, S.P. Solodovnikov, I.S. Belostotskaya, V.V. Ershov, and M.I. Kabachnik, Dokl. Akad. Nauk SSSR (in the Press).

in radicals (VII)–(XI) (solvent—toluene) is illustrated below:

Radical	Acyl	$10^{-4}\nu(20°)$, s^{-1}	$10^{-12}\nu_0$, s^{-1}	E_{act} ± 1.0, kcal mole^{-1}
(VII)	$COCH_3$	1	9.0	11.4
(VIII)	COC_2H_5	1	11.0	13.0
(IX)	$COCH_2Br$	26	21.0	10.7
(X)	$COCH_2C_6H_5$	10	0.6	9.15
(XI)	$COCH(C_6H_5)_2$	3	2.3	10.7

Evidently, as the electron-accepting properties of the substituents in the acyl group become more pronounced, the exchange frequencies increase and the energy barriers diminish. The data for radicals (X) and (XI) show that the mass of the migrating fragment plays a definite role. The results suggest that the facilitation of the migration of the acyl group following the enhancement of the electron-accepting properties of the substituents is due to the electron deficiency arising at the carbonyl carbon atom, which favours the formation of a polar transition state. The migration of acyl groups apparently proceeds via this state. The above mechanism of acylotropic migration is supported by positive acid catalysis. It has been shown for radical (VII)[61] that in the presence of one mole of trifluoroacetic acid the energy barrier decreases by a factor of two, and the frequency of migration of the acyl group increases by a factor greater than 100. The electron deficiency at the carbonyl carbon atom occurs as a result of the protonation of the carbonyl group in the acid–radical complex.

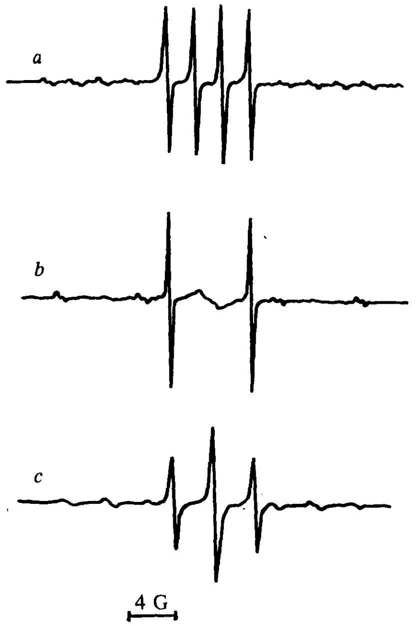
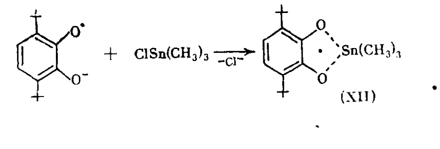


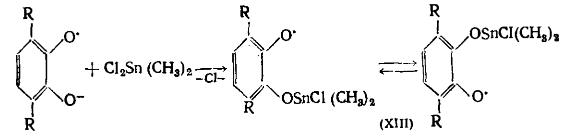
Figure 13. The EPR spectra of radical (XIII) in THF at different temperatures (°C): *a*) −70; *b*) 0; *c*) 110.

Radicals containing the trimethylstannyl group have been obtained by the reaction of 3,6-di-t-butyl-*o*-semiquinone radical-anions with chlorotrimethylstannane[62]:



The EPR spectrum of this radical is a triplet with a_H = 3.6 G due to the equivalent ring protons. In addition, the lines due to the paramagnetic tin isotopes are observed ($a_{^{117}Sn}$ = 12.8 G and $a_{^{119}Sn}$ = 13.3 G). Variation of temperature does not lead to a specific broadening of the spectral lines, which indicates either a stationary symmetrical disposition of the tin-containing group or its rapid migration (relative to the EPR time scale) between the oxygen atoms.

Stannotropic transitions, revealed by EPR spectra, have been observed in radical (XIII), obtained by the interaction of the semiquinone radical-anion with dichlorodimethylstannane[62]:



(R = t-butyl) .

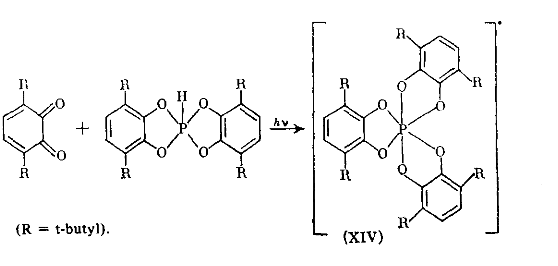
Fig. 13 shows that, as the temperature is reduced from 110° to −70°C, the EPR spectra of radical (XIII) reveal a transition from the triplet with a_H = 3.6 G, due to the HFI of the equivalent aromatic ring protons, to a doublet of doublets (a_H = 5.2 G, a_H = 2.6 G), which indicates the breakdown of the "equivalence" of the ring protons. An alternation of line widths, due to the intramolecular migration of the tin-containing fragment, is observed in the intermediate temperature range. The kinetic parameters of the tautomerism of radicals (VI), (XII), and (XIII) in THF are presented below:

Migrating radical	$\nu(20°)$, s^{-1}	$10^{-12}\nu_0$, s^{-1}	E_{act} ± 0.5 kcal mole^{-1}
(VI) $-CH_3$	0	—	—
(XII) $-Sn(CH_3)_3$	10^9	—	—
(XIII) $-Sn(CH_3)_2Cl$	$9 \cdot 10^6$	50	9.1

The data presented permit a quantitative comparison of the migration frequencies of fragments containing Group IV elements. The increase of migration frequency on passing from carbon to tin [radicals (VI), (XII), and (XIII)] illustrates the decisive role of the coordination unsaturation of the central atom of the migrating fragment in tautomeric transitions.

3. Free Radicals with a Six-Coordinated Phosphorus Atom

The above examples constitute "two-well" tautomeric systems (migration of fragments between two oxygen atoms). We shall now examine more complex instances of degenerate tautomerism, where the free valence migrates between six or four oxygen atoms ("wandering" valence). Such radicals have been obtained as a result of the interaction of 3,6-di-t-butyl-*o*-quinone with tetra-t-butylspirophosphorane under the influence of ultraviolet radiation. This interaction can be represented as follows[63]:



(R = t-butyl).

At high temperatures the EPR spectrum of radical (XIV) is a doublet due to the interaction of the unpaired electron with the ^{31}P nucleus (a_P = 4.1 G). Each component of the doublet contains seven lines (a_H = 1.45 G), the intensity ratios of which indicate unambiguously the interaction of the unpaired electron with six "equivalent" ring protons (Fig. 14*a*). With decrease of temperature, the HFS components with the proton nuclear spin projections $M_I = \pm 2$, ± 1 are broadened (Figs. 14*b*, 14*c*, and 14*d*) and at fairly low temperatures (−80° C) a spectrum is recorded in which each component of the phosphorus doublet contains three lines (a_H = 4.35 G) (Fig. 15*e*) corresponding to the interaction of the unpaired electron with two equivalent protons in a single ring. The above changes in the spectra are fully reversible with respect to temperature; the constant for hyperfine interaction with the ring protons is smaller by a factor of three in the high-temperature spectra than in those at low temperatures (Fig. 14).

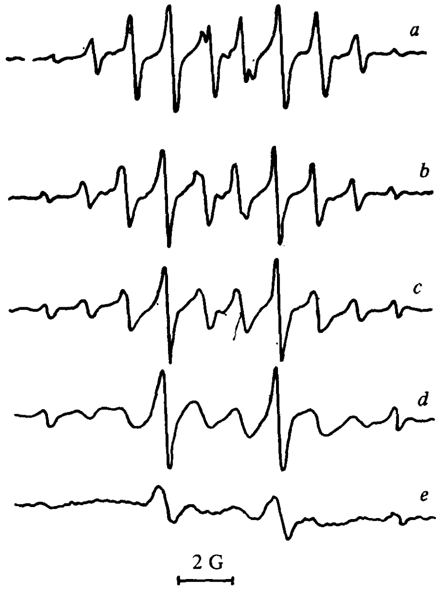
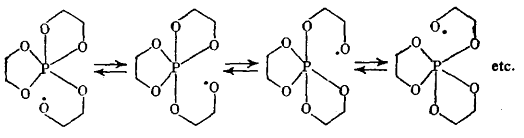


Figure 14. The EPR spectra of radical (XIV) in toluene at different temperatures (°C): *a*) 0; *b*) −20; *c*) −40; *d*) −60; *e*) −80.

In interpreting the results one must bear in mind that the high-temperature spectra indicate the presence of six equivalent protons in radical (XIV). Since a specific broadening of the components of the septet, indicating the occurrence of dynamic effects, is observed when the temperature is reduced, presumably the "equivalence" of the six protons at high temperatures is achieved as a result of rapid exchange of the free valence and a bond in the system:



The free valence then "runs round" all six oxygen atoms of the catechol ligands and, in terms of the EPR scale, the phosphorus atom has a coordination number of six.

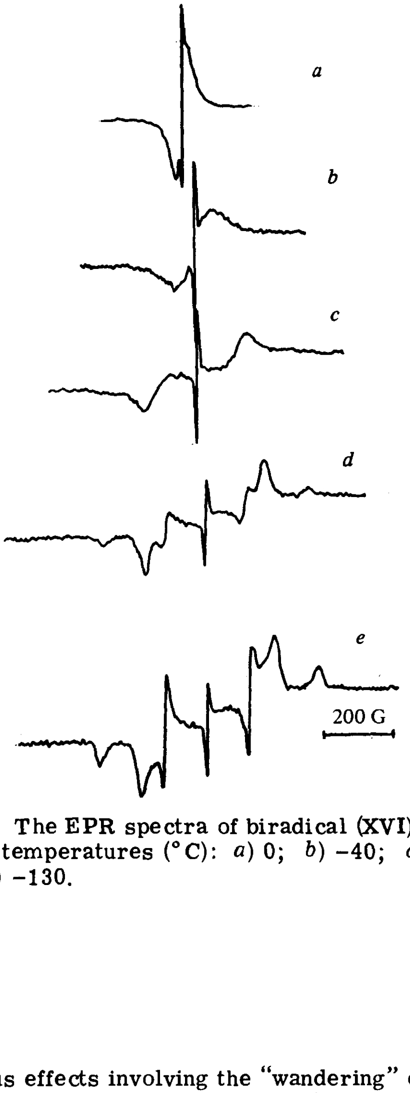
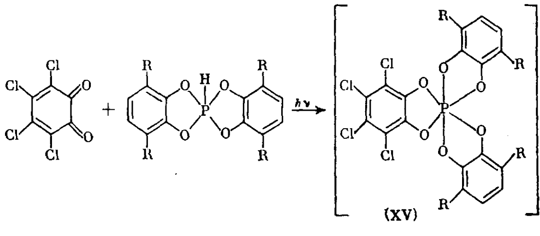


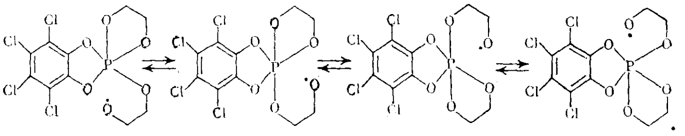
Figure 15. The EPR spectra of biradical (XVI) in toluene at different temperatures (°C): *a*) 0; *b*) −40; *c*) −80; *d*) −100; *e*) −130.

Analogous effects involving the "wandering" of the free valence have been obtained for radical (XV):



(XV)

At high temperatures each component of the phosphorus doublet contains five lines owing to the four protons of the two 3,6-di-t-butylcatechol ligands, which indicates the exchange of the unpaired electron and a bond between these ligands. The delocalisation of the unpaired electron over the two catechol ligands makes the HFI constant for the ring protons greater by a factor of 1.5 than in radical (XV) and indicates the absence of the exchange of the unpaired electron and a bond in the *o*-chloranil ligand:



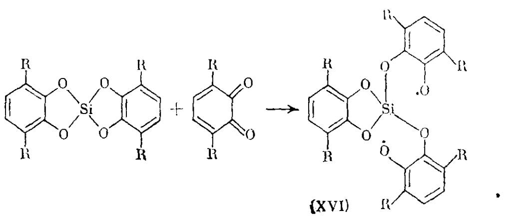
Analysis of line widths made it possible to estimate the energy parameters of the "wandering" of the free valence, the general expressions for which are as follows in the case of radicals (**XIV**) and (**XV**):

$$\nu_{\text{XIV}},\ (\text{s}^{-1}) = 3{,}4\cdot 10^{12}\exp[-(4{,}3 \pm 0{,}5)/RT],$$
$$\nu_{\text{XV}},\ (\text{s}^{-1}) = 0.9\cdot 10^{12}\exp[-(3.6 \pm 0.5)/RT].$$

At 20° C the frequencies of the "wandering" of the free valence in these radicals are similar and amount to 2×10^9 s^{-1}.

4. Free Radicals with a Six-Coordinated Silicon Atom

The effects associated with the intramolecular exchange of an electron and a bond in multiwell systems, which we have referred to as the "wandering" of the free valence, have been observed for free radicals with a six-coordinated silicon atom. Such radicals have been obtained by the interaction of silicon bis-3,6-di-t-butylcatecholate with 3,6-di-t-butyl-*o*-quinone, which leads to the formation of biradicals[64]:



(XVI)

The EPR spectra obtained for frozen solutions of these species are characteristic of biradical systems (Fig. 15) with an effective spin–spin interaction of two unpaired electrons, manifested by the presence of the zero splitting constants *D* and *E*. On raising the temperature, the spin–spin interaction is averaged out and the EPR spectrum of the liquid phase consists of a single broad line, which narrows on raising the temperature (Fig. 15). The line width between the points of maximum slope at 20° C is 25 G. Such a change in the spectra is characteristic of stable biradicals of the phenoxy-type and confirms the proposed structure of the species formed[23]. At half-field (g = 4) an intense absorption is observed (in frozen solutions), corresponding to a transition with $\Delta m = \pm 2$ and persisting down to −80° C.

Analysis of the main spectrum (Fig. 15*e*) gave the zero splitting parameters $D = 322$ G and $E = 24$ G. The non-zero value of *E* indicates the absence of axial symmetry in the unpaired electron distribution in biradical (XVI). The constant *D* characterises the average distance between the spins and, in terms of the point dipole approximation, is defined by the expression $D = g\beta r_{\text{av}}^{-3}$. One must bear in mind that the unpaired electrons are delocalised over the conjugated bond system of the catechol rings and, for small distances between the radical centres, comparable with the unpaired electron delocalisation regions, the point model may prove to be inapplicable to the estimation of distances between the interacting spins.

The parameter *D* depends greatly on r_{av}, so that one may assume that the main contribution to *D* comes from the spin density ρ_0 at the oxygen atoms of biradical (**XVI**) capable of maximum mutual approach. The estimate of the distribution of spin density in the 3,6-di-t-butyl-2-hydroxyphenoxy-radical[65], whose structure is similar to that of the radical fragments of biradical (XVI), suggests that $\rho_0 = 0.3$, so that $r_{\text{av}} = 3$ Å. If biradical (XVI) has a "quasi-octahedral" configuration owing to the coordination of the unpaired electrons to the vacant orbitals of silicon, then the univalent oxygen atoms may be either in the *cis*- or *trans*-positions relative to one another. The *trans*-positions for normal SiO bonds are separated by a distance of 3.3 Å. For coordinate bonds, these distances are apparently greater, and one may therefore assume that the distance $r = 3$ Å in biradical (XVI) corresponds to the *cis*-positions of the "univalent" oxygen atoms. This is confirmed by the absence of axial symmetry ($E \neq 0$) in the spectra of frozen solutions.

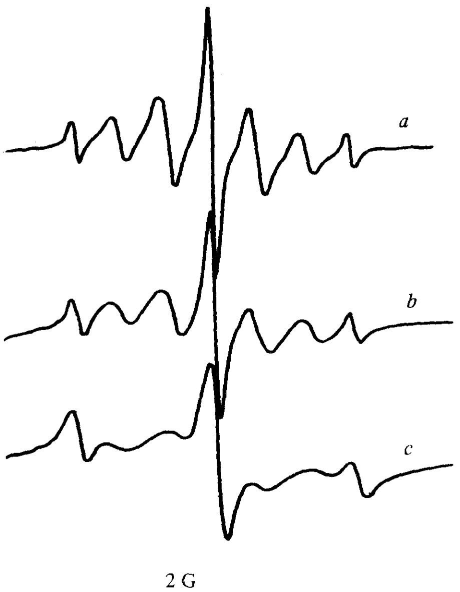
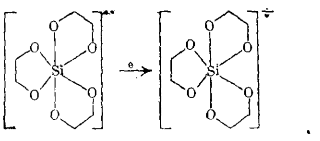


Figure 16. The EPR spectra of radical (XVII) in THF at different temperatures (°C): *a*) −40; *b*) −60; *c*) −80.

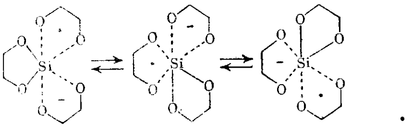
The main evidence for the structure of biradical (XVI) was the spectroscopic detection of the radical-anion (XVII), obtained by the electrochemical reduction of biradical (XVI):



(XVI) (XVII)

Fig. 16 presents the EPR spectrum of radical-anion (XVII) in THF, which consists at low temperatures (−80° C) of three lines due to the interaction of the unpaired electron with two protons in a single catechol ligand ($a_{\text{H}} = 3.75$ G).

With increase of temperature, additional broad lines appear in the spectrum, becoming narrower on further heating (Figs. 16*a* and 16*b*) and indicating the interaction of the unpaired electron with six "equivalent" protons and three catechol rings (a_H = 1.25 G). The above changes are fully reversible when the temperature is altered and indicate intramolecular processes. These reduce to the "wandering" of the free valence and the charge in accordance with the mechanism



The electronic structure of radical-anion (XVII) differs from that of the usual radical-anions obtained on reduction of neutral organic compounds. In the ion pairs formed by the latter compounds the motion of the cation is indissolubly linked to the synchronous redistribution of the charge and spin intensities of the unpaired electron over the system of conjugated bonds (for example in semiquinone radical-anions, see Section III). In ion pairs formed by radical-anion (XVII) the charge and spin densities are in principle separate and localised in different ligands. Under these conditions, the migration of the cation (and the redistribution of charge density) may take place to some extent independently of the exchange of the free valence and a bond, as can be seen from an examination of the "instantaneous" structures of ion pairs formed by radical-anion (XVII):

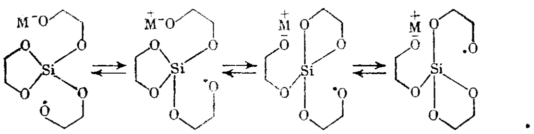


Table 2. The kinetic parameters of the interligand electron exchange in ion pairs comprising radical-anion (XVII).

Cation	Solvent	10^{-6} ν (20°), s^{-1}	$10^{11}\nu_0$, s^{-1}	E_{act} ± 0.5 kcal mole^{-1}
TBA^+	THF	10^3	10	4.1
Na^+	THF + crown	$4\cdot10^2$	10	4.6
Na^+	THF	2.5	7.4	7.4
Na^+	DME	2.2	22	8.1
K^+	THF	1.8	1.5	6.6
K^+	DME	1.2	7	7.9
Li^+	THF	0.6	$3\cdot10^{-4}$	2.3
Li^+	DME	1.1	0.12	5.5

Note. TBA^+ is the tetrabutylammonium cation and crown stands for 18-crown-6 (0.01 M).

The characteristics of the structure of ion pairs formed by radical-anion (XVII) are clearly manifested in the variation of the frequency of the exchange (ν_{exch}) of the unpaired electron and a bond as a function of temperature, the nature of the cation, and the solvating properties of the medium (Table 2). In the free radical-anions (XVII) (tetrabutylammonium cation) and in alkali metal salts of radical-anion (XVII) in the presence of crown-ethers, which are powerful solvating agents, the kinetic parameters of the exchange are large and close to the values for radical (XIV) with a six-coordinated phosphorus atom, which has a similar structure but no negative charge. This supports the view that the rate-limiting stage of the interligand electron exchange in these species is the exchange of the free valence and a bond, i.e. an intramolecular radical substitution reaction.

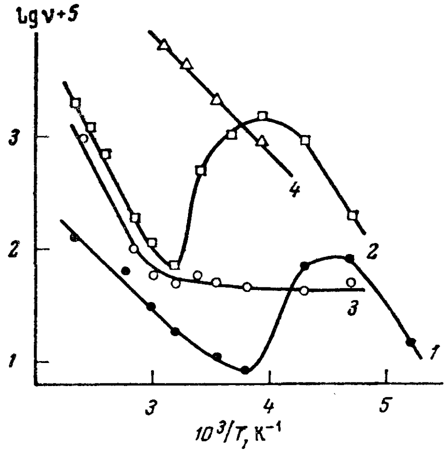


Figure 17. Dependence of the exchange frequency in radical-anion (XVII) on $1/T$ in DME for different cations: 1) Li^+; 2) Na^+; 3) K^+; 4) t-butylammonium.

Table 2 shows that in contact ion pairs formed by radical-anion (XVII) (alkali metal cations, weakly solvating solvents) ν_{exch} is appreciably lower and its temperature dependence in terms of Arrhenius coordinates is non-linear (Fig. 17). The rate-limiting stage of the exchange in contact ion pairs is the migration of a cation from ligand to ligand and a non-linear Arrhenius temperature dependence of ν_{exch} is due to the competition of two processes: the solvation of the cation by solvent molecules, responsible for the approach to the properties of free ions and the acceleration of the exchange frequency (low temperatures), and to the increase with temperature of the fraction of contact ion pairs in which the exchange frequency is much lower than in the solvated complexes. This competition in fact leads to the observed results: with increase of temperature, the exchange frequency initially falls and then increases again at very high temperatures (Fig. 18).

A characteristic feature of the exchange of the free valence and a bond in radical-anion (XVII) is the transition from the intraligand exchange immediately to the three-ligand exchange, bypassing the two-ligand exchange stage, which can be formally postulated on the basis of the above examination of the "instantaneous" structures of radical-anion (XVII). This can be explained by the fact that in contact ion pairs formed by radical-anion (XVII), where the unpaired electron is localised in one ligand, the cation tends to assume a symmetrical disposition relative to the other two catechol rings, determined by the coordination of the lone electron pairs of the oxygen atoms in the field of the cation (by analogy with crown-ethers). Such coordination prevents the involvement of the "vacant" ligand in the two-ligand exchange and creates conditions for the involvement of all three ligands at once in the exchange process. This also explains why the migration of the cation is rate-limiting in the exchange of the free valence and a bond in contact ion pairs[66].

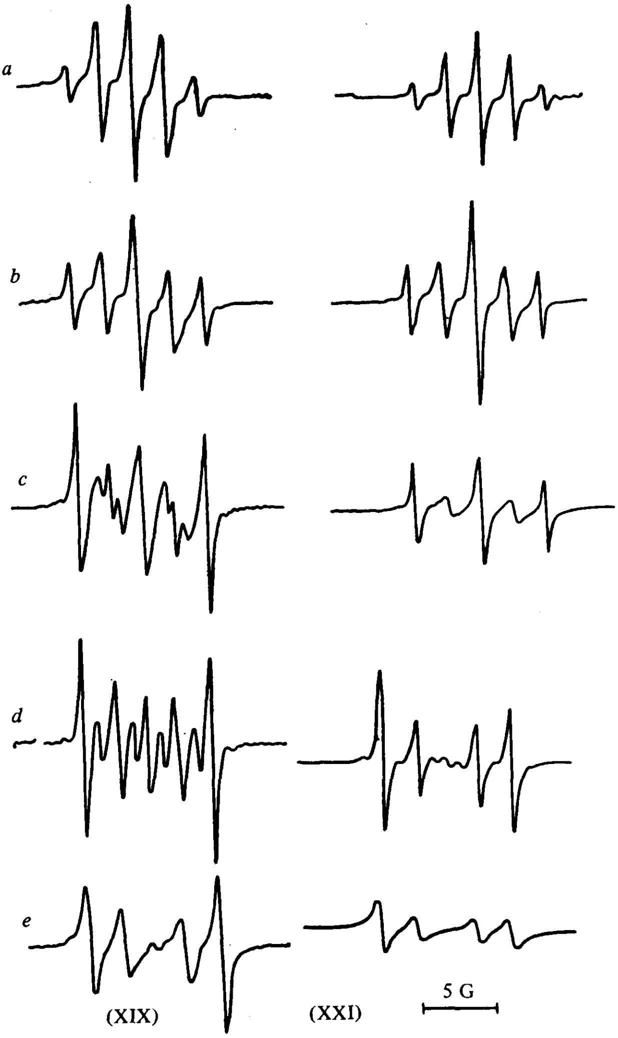
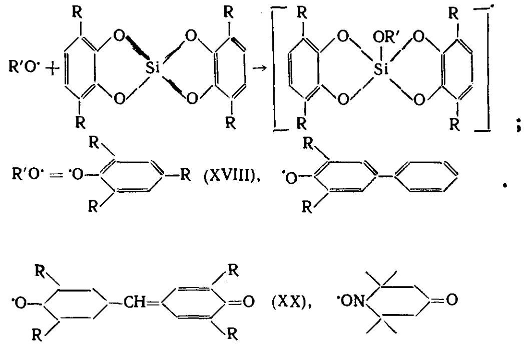


Figure 18. The EPR spectra of radicals (XIX) and (XXI) in pentane at different temperatures (°C): *a*) 80; *b*) 40; *c*) -40; *d*) -80; *e*) -110.

5. Free Radicals with a Five-Coordinated Silicon Atom

The two-ligand exchange of the unpaired electron and a bond has been investigated in detail in relation to free radicals with a five-coordinated silicon atom, obtained by the interaction of stable phenoxy- and iminoxy-radicals with silicon bis-(3,6-di-t-butylcatecholate) (SC)[67]:



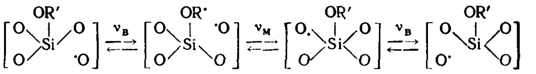
(XIX)

(XXI)

The kinetic parameters of the exchange between the electron and a bond in radicals with a five-coordinated silicon atom in pentane are listed below:

Radical	$10^{-8}\nu(20°)$, s^{-1}	$10^{-11}\nu_0$, s^{-1}	$E_{act} \pm 0.5$, kcal $mole^{-1}$
(XVIII) — (XX)	22	44	4.5
(XXI)	4.5	4.2	4.1

At high temperatures (80°C) the spectra of these radicals consist of a quintet (Fig. 18), due to the interaction of the four "equivalent" protons of the two catechol rings (a_H = 2.19 G), the silicon atom has a coordination number of five in terms of the EPR time scale, and the unpaired electron "runs round" the four oxygen atoms in the two catechol rings with a high frequency ("wandering" valence):



In other words, the rapid exchange condition is fulfilled; ν_B and ν_M are the frequencies of the exchange of the unpaired electron and a bond within a single ligand and between ligands respectively.

It is striking that the exchange does not involve the Si–OR bond, where it is possible to specify formally a state corresponding to the initial reactants (RO· and SC). It has been shown for radical (XXI) that at high temperatures (in excess of 100°C) this state does exist, but it corresponds simply to the reverse dissociation of radical (XXI) and the EPR spectra show a decrease of the intensity of the (XXI) lines and the appearance of the spectrum of the initial iminoxy-radical. At lower temperatures the equilibrium is wholly displaced towards radical (XXI) and the exchange takes place only between the catechol ligands and within them (the quintet due to the four "equivalent" protons of the two catechol rings). The alternative hypothesis of the possible ionic character of the Si–OR bond is unlikely, because the ultraviolet spectra of radicals (XVIII)–(XXI) obtained lack bands characteristic of the RO^- anion.

With decrease of temperature, the components of the quintet with M_I = 0, ±1, are broadened, which indicates inhibition of the exchange (Figs. 18*b* and 18*c*). At low temperatures (-110°C) the spectrum consists of a doublet (a_4^H = 6.37 G), each component of which is split into two lines (a_5^H = 2.37 G) (Fig. 18*e*) and corresponds to the structure with the localisation of the unpaired electron at one oxygen atom of the catechol ligand (slow exchange condition fulfilled)[67]. The HFI constants were assigned on the basis of the generally accepted ideas, according to which the maximum HFI is due to the proton in the *para*-position relative to the univalent oxygen atom.

The kinetic parameters of the exchange of the unpaired electron and a bond were estimated from the broadening of the central component of the quintet (relative to the extreme components) and reflect the change in the exchange frequency as a function of the nature of the added radical and the solvent. In pentane the frequencies and the energy barriers estimated in this way are similar for all radicals (see above).

In the intermediate exchange frequency range ($\nu_B, \nu_M \simeq \gamma_e\Delta a$) the alternation of line widths in the EPR spectra of radicals (XVIII)–(XXI) has its characteristic features. Firstly, the central component ($M_I = 0$) and lines with $M_I = \pm 1$ in the quintet are broadened non-uniformly and their intensity ratios change from 4 : 6 : 4 (high temperatures) to 1 : 2 : 1 (when the temperature is reduced—Figs. 18*a*, 18*b*, and 18*c*), and in certain cases even as far as 1 : 3 : 1.[67] On further reduction of temperature, the central component becomes less intense than the lateral ones ($M_I = \pm 1$) and additional lines appear, vanishing as a result of a further reduction of temperature accompanied by the formation of a doublet of doublets (Figs. 18*c*, 18*d*, and 18*e*).

Before analysing these features, it is necessary to examine the individual contributions to the line widths taking into account the intra- and inter-ligand exchange processes as the intermediate stages in the inhibition of the overall exchange in the course of the localisation of the unpaired electron at one of the oxygen atoms (Fig. 19). From this standpoint, the radicals investigated may be regarded as "four-well" systems with potential energy minima for each of the four oxygen atoms. This system can be formally divided into two types of "two-well" subsystems, in the first of which the exchange of the electron and a bond takes place in a single ligand [intraligand exchange (ν_B)]. For this exchange, the EPR spectrum should consist of a triplet due to the interaction of the unpaired electron with the two "equivalent" protons of a single catechol ring; the HFI constant for this triplet is equal to half the sum of the HFI constants for the limiting structure (Fig. 19). The second type involves exchange between the oxygen atoms of different ligands [interligand exchange (ν_M)]. This case should give rise to a spectrum consisting of a triplet due to the presence of two *para*-protons (the 4-position relative to the univalent oxygen atom); its HFI constant is equal to half the HFI constant for the *para*-proton in the limiting structure. Each component of this triplet contains three lines due to the *meta*-protons (the 5-positions in the two-ligands) with an HFI constant equal to half the constant for the *meta*-proton in the limiting structure (Fig. 19).

One can imagine that the inhibition of the overall exchange (the conversion of the quintet into a doublet of doublets) proceeds via preliminary stages involving complete inhibition of one of the types of migration: type I with $\nu_B \gg \nu_M$ and type II with $\nu_B \ll \nu_M$. In these cases the spectrum should vary in accordance with the schemes in Fig. 19 with the intermediate formation of a triplet and a triplet of triplets respectively. However, the experimental spectra are complex (Fig. 18), which necessitates the hypothesis that both types of migration occur simultaneously in radicals (XVIII)–(XXI).

To test this hypothesis, the contributions to the width of the quintet $\Delta(T_2^{-1})$ were calculated for the two cases considered[67]. Evidently, whereas the broadening of the central component of the triplet is the same for both types of inhibition of the exchange, for the components with $M_I = \pm 1$ the broadening is different in each case. We calculated these contributions using the HFI constants for the limiting structures of the radicals investigated. Table 3 (type I) shows that four lines of the central component make a minimal contribution (16 G) compared with the lines having $M_I = \pm 1$ (35 G). This explains the non-uniform broadening of the components, mentioned above. The sharp decrease of the intensity of the central component on further reduction of temperature may be due to the predominance of the type II inhibition ($\nu_B \ll \nu_M$). Indeed in this case the minimal contribution to the broadening comes from the lines with $M_I = \pm 1$ (9.6 G) compared with the central component (16 G). This is also supported by the appearance of additional lines (the formation of a nine-line spectrum) on further reduction of temperature (Figs. 18*c* and 18*d*), which may be attributed to the intermediate formation of a triplet of triplets (cf the scheme in Fig. 19). The discrepancy between the intensities may be due to the non-rigorous fulfilment of the rapid exchange condition for the individual components at a particular exchange frequency (different contributions to the width) and also to the presence of an intermediate spectrum of the exchange inhibition type (a triplet, Fig. 19).

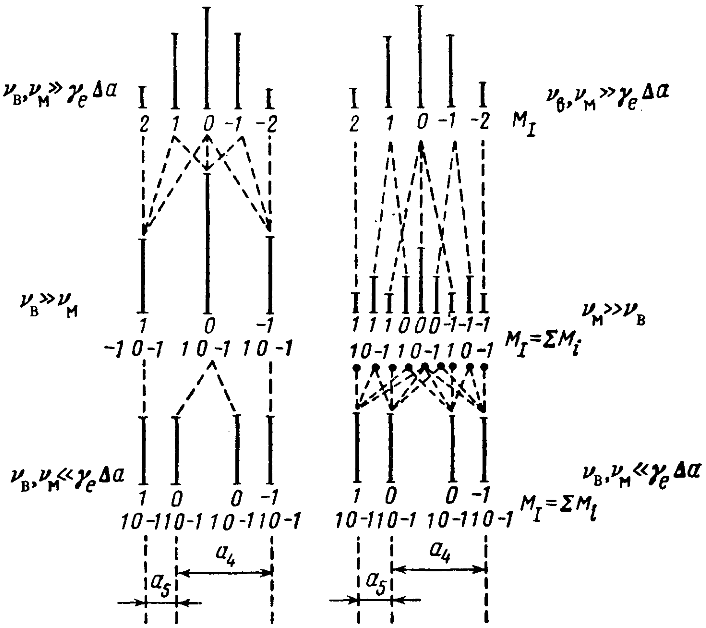
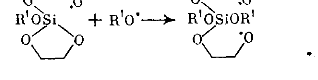


Figure 19. Schematic representation of the spectra of radicals (XVIII)–(XXI) under the conditions of the inhibition of the interligand exchange (type I) and the intraligand exchange (type II).

The increase of the thermodynamic stability of radicals (XVIII)–(XXI) after their formation suggests that they can combine with yet another initial radical to form the corresponding biradicals. Such species are produced when SC is made to react with an excess of the initial radicals:



Under these conditions, the EPR spectra shows signals characteristic of biradical systems; analysis of the spectrum makes it possible to determine the zero splitting constants for the biradicals (D = 335 ± 8 G, E = 21 ± 2 G). Estimates of the distances between the unpaired electrons yield 2.9 Å, which indicates the coordination of the unpaired electrons to the vacant orbitals of silicon. In frozen solutions signals at half-field (g = 4) are also recorded and at the usual temperatures signals in the form of single broad lines have been observed.

Table 3. The contributions $\Delta(T_2^{-1})$ to the width of the components of the quintet in the spectra of radicals (XVIII)-(XXI) under conditions of the inhibition of the exchange of the unpaired electron and a bond. (The numerical contributions were obtained with the following HFI constants: a_4^H = 6.37 G and a_5^H = 2.37 G).

Fast exchange				Intermediate exchange			
				type I exchange, $\nu_B \gg \nu_M$		type II exchange, $\nu_B \ll \nu_M$	
M_I	degeneracy	$M_I = \Sigma M_i$	degeneracy	$\Delta(T_2^{-1})$	$\Delta(T_2^{-1})$, G²	$\Delta(T_2^{-1})$	$\Delta(T_2^{-1})$, G²
±2	1	±1, ±1	1	0	0	0	0
±1	4	±1, 0	2	$^1/_4(a_4+a_5)^2+(a_4-a_5)^2$	35	$^1/_4(a_4-a_5)^2+a_5^2$	9.6
		0, ±1	2	$^1/_4(a_4+a_5)^2+(a_4-a_5)^2$	35	$^1/_4(a_4-a_5)^2+a_4^2$	44.5
0	6	0, 0	2	$(a_4+a_5)^2$	76.5	$(a_4+a_5)^2$	76.5
		±1, ±1	4	$(a_4+a_5)^2$	16	$(a_4-a_5)^2$	16

Table 4. The spectroscopic parameters of radicals (XXII) and (XXIII).

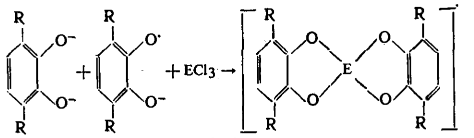
Radical	Element (E)	Content,%	I	$\overset{\bullet}{\nu}_\mu$	a_E, G	a_H, G	
						slow exchange	fast exchange
(XXII)	^{11}B	81.3	3/2	29	2.5	4.5	2.25
	^{10}B	18.8	3	9.7	0.83	4.5	—
(XXIII)	^{27}Al	100	5/2	23.5	2.58	4.0	2.0

---

*The magnetic moments are expressed in terms of the NMR frequencies for a constant field of 21.14 kG.

6. Free Radicals with Four-Coordinated Boron and Aluminium Atoms

The effects associated with the "wandering" of the free valence have been observed also for radicals with four-coordinated boron and aluminium atoms, obtained as a result of the following reaction[68]:



;

E = B (XXII), or Al (XXIII) .

The EPR spectrum of the boron-containing radical (XXII) is a quartet (Fig. 20), due to the interaction of the unpaired electron with the main paramagnetic ^{11}B isotope (Table 4).

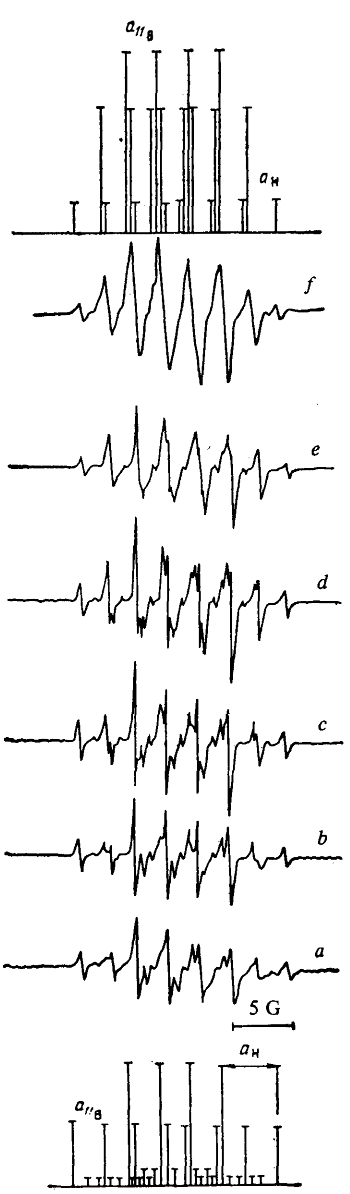


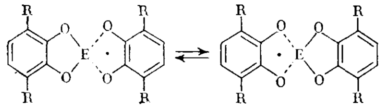
Figure 20. The EPR spectra of radicals (XXII) in THF at different temperatures (°C): a) −100; b) −80; c) −60; d) −40; e) −20; f) 20; data obtained from the reconstruction of the spectra corresponding to high and low temperatures and obtained with the HFI constants listed in Table 4.

Each component of this quartet consists at low temperatures (−100° C) of a triplet (1 : 2 : 1) due to two protons of a single catechol ring (Fig. 20a). In addition, lines due to the ^{10}B isotope can be observed in the spectra at low temperatures. The ratios of the constants for the interaction of the unpaired electron with paramagnetic boron isotopes ($a_{^{11}\mathrm{B}}/a_{^{10}\mathrm{B}} = 3$) and the intensity ratio of the corresponding lines ($I_{^{11}\mathrm{B}}/I_{^{10}\mathrm{B}} = 7.5$) agree satisfactorily with the values calculated theoretically on the basis of the analysis of the magnetic moments of the nuclei and the natural abundances of the two isotopes (3 and 7.6 respectively).

When the specimen is heated, additional broad lines, narrowing on further increase of temperature (Figs. 20*b*, 20*c*, and 20*d*), are observed. At 20° C and above, each component of the boron quartet is transformed into a quintet with binomial intensity ratios (Fig. 20*e*) due to the interaction of the unpaired electron with the four equivalent protons of the two catechol rings. The changes in the spectra are fully reversible with respect to temperature and the HFI constant for the quintet is smaller by a factor of two than for the triplet at low temperatures.

Analogous changes occur in the EPR spectra of radical (XXIII), which has a central aluminium atom. Its spectra are illustrated in Fig. 21 and confirm the proposed structure. Six lines are due to the ^{27}Al nucleus (Table 4) and each component of the sextet consists of a triplet (low temperatures, Fig. 21*a*) or a quintet (high temperatures, Fig. 21*e*) due to the interaction of the unpaired electron with the protons of one or two catechol rings respectively.

The observed dynamic effects in the EPR spectra of radicals (XXII) and (XXIII) indicate rapid exchange of the free valence and a bond in these radicals:



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At high temperatures the free valence "runs round" the four oxygen atoms and the B and Al atoms have tetrahedral configurations in terms of the EPR time scale. As for the free radicals with a six-coordinated phosphorus atom, the barriers to the transition within a single ligand are overcome at low temperatures and the unpaired electron interacts with the protons of a single ring[68].

Analysis of line widths made it possible to estimate the kinetic parameters of the "wandering" of the free valence, the general expressions for which are of the following form in the case of radicals (XXII) and (XXIII):

$$\nu_{\mathrm{XXII}},\ (\mathrm{s}^{-1}) = 1{,}8\cdot 10^{13}\exp[-(4200 \pm 300)/RT],$$

$$\nu_{\mathrm{XXIII}},\ (\mathrm{s}^{-1}) = 3.2\cdot 10^{11}\exp[-(3000 \pm 300)/RT].$$

At 20°C we have $\nu_{\mathrm{XXII}} = 2 \times 10^{9}\ \mathrm{s}^{-1}$ and $\nu_{\mathrm{XXIII}} = 1.25 \times 10^{10}\ \mathrm{s}^{-1}$.

Thus the spectroscopic data obtained constitute convincing evidence in support of the structures proposed for the radicals under consideration and illustrate the existence in the latter of a "wandering" valence in the presence of four-coordinated boron and aluminium atoms. The differences between the frequencies and the exchange of the free valence and a bond in these radicals are apparently due to the difference between the types of element–oxygen bonds.

The processes associated with degenerate tautomerism considered above can serve, depending on the type of migrating species, as models of heterolytic (cationotropism) and homolytic (intramolecular radical substitution) reactions. The study of the ion pairs formed by radical-anions, cationotropic processes, and the solvation of ions has greatly extended our ideas about the occurrence of ionic processes in organic solvents.

The conclusion that the mobility of the cation plays an important role in intramolecular electron transfer processes we believe to have a more general importance, going outside the limits of the chemistry of radical-anions. The idea that certain reactions proceed via an electron transfer stage is being developed at the present time[69,70]. In those cases where compounds containing alkali or other metal cations, for example, organometallic compounds, alkoxides, radical-anions, etc. serve as electron donors it is necessary to take into account the role of dissociative processes, without which it is impossible to describe correctly the electron transfer processes.

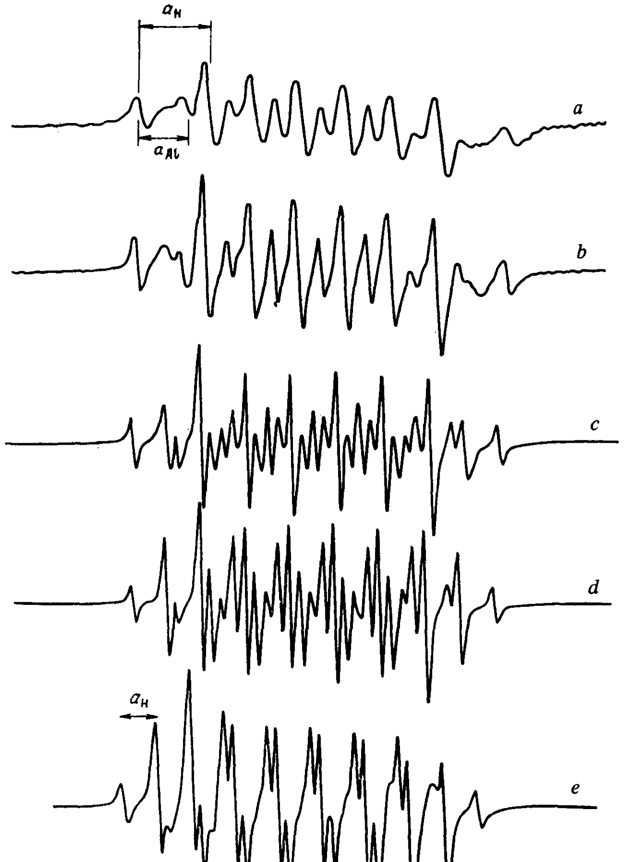

Figure 21. The EPR spectra of radical (XXIII) in THF at different temperatures (°C): *a*) −110; *b*) −100; *c*) −80; *d*) −40; *e*) 0.

The above examples of the tautomerism of radicals illustrate a type of tautomeric transformation new to organic chemistry, which constitute in essence intramolecular radical substitution reactions and permits certain generalisations concerning factors influencing the frequency of the transfer of the migrating fragments. In the simplest instances (migration of hydrogen and deuterium) it is evident that the formation of an intramolecular hydrogen bond intensifies the tendency of these atoms to assume a symmetrical disposition relative to the oxygen atoms of the catechol ring (the difference between the lengths of the normal and hydrogen bonds for the planar disposition of the O...HO fragment is only 0.3 Å[57]). The introduction of solvents capable of forming hydrogen bonds inhibits the migration of hydrogen owing to the competitive effects involving the formation of intermolecular hydrogen bonds by these solvents with the proton of the hydroxy-group.

In all the remaining cases considered the electron deficiency at the central atom of the migrating fragment promotes the coordination of the "univalent" oxygen to the vacant orbitals of this atom, which leads to high frequencies of the tautomeric transitions observed by the EPR method (10^6-10^{10} s^{-1}).

The tautomeric transformations in free radicals with four-, five-, and six-coordinated atoms of Group III, IV, and V elements ("wandering" valence) constitute in essence a new type of delocalisation of the unpaired electron namely delocalisation with bond dissociation. The data obtained suggest that analogous effects should be observed in the corresponding diamagnetic anions and should be associated with the "wandering" of the charge at a frequency which depends significantly on the state of the ion pairs involving these anions.

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Solid-phase Radical Reactions and Mechanism of Oxidation of Carbon-chain Polymers

E.T.Denisov

Analysis of recent results on the kinetics of the oxidation of model hydrocarbons and carbon-chain polymers in solution and in the solid phase emphasises the common character of the oxidation mechanisms in liquid and solid phases. Detailed consideration is given to specific features of the solid-phase oxidation of polymers consequent on their high molecular mass, inhomogeneity in the solid state, the influence of molecular mobility on the kinetics of radical reactions, and the migration of free electrons. A list of 104 references is included.

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I. INTRODUCTION

The history of science contains many examples of how, with the development of theory and experiment, research workers pass from studying comparatively simple to increasingly complicated systems, a tendency that can be traced in the kinetics of chain oxidations. Semenov's theory of branched and degenerate chain reactions was based on the gas-phase oxidation of simple molecules[1]. The oxidation of hydrocarbons and aldehydes in the gas phase occupied a central position in kinetic research during the 1930s and 1940s.[2] Advance into the liquid-phase oxidation of hydrocarbons was a feature of kinetic investigations during the 1950s,[3] which was subsequently applied to diverse organic compounds[4]. During the past decade the interest taken by research workers in the mechanism of the oxidation of polymers has grown considerably, both in our own country[5,6] and abroad[7-9]. The number of publications devoted to oxidation and radical reactions in polymers approaches the number on liquid-phase oxidation and far exceeds the annual number on gas-phase oxidation. Some of the apparent reasons for this change in the direction of research are enumerated below.

Firstly, the theory of the oxidation of polymers forms the scientific basis for their stabilisation and for predicting the durability of polymeric materials.

Secondly, the oxidation of polymers relates to a complicated, interesting, and hitherto largely unsolved scientific problem—the kinetics of radical reactions in the solid phase—and thus to the radiation chemistry of polymers and solid-phase polymerisation.

Thirdly, quantitative kinetic methods, developed earlier in the study of the liquid-phase oxidation of hydrocarbons, have been more and more widely used in research on the oxidation of polymers. Results obtained by these methods permit in several cases a quantitative comparison with the liquid-phase oxidation of model hydrocarbons.

Fourthly, very valuable results have recently been obtained on the oxidation of polymers in solution. Electron spin resonance has been widely used to measure the rate constants of radical reactions[10,11]. It has revealed the polychromatic kinetics of radical reactions in the solid phase[11] and the dependence of the rate of the primary step on the rigidity of the polymer matrix[12].

Comparison of experimental results obtained during recent years on the oxidation of polymers with data on the liquid-phase oxidation of model hydrocarbons indicates the similarities and differences between solid-phase and liquid-phase oxidation, together with possible reasons for such differences. These aspects will be covered in the present Review.

II. OXIDATION OF POLYMERS IN SOLUTION

The liquid-phase chain oxidation of hydrocarbons[3] and other organic compounds[4] involves the following primary stages

$$\text{Initiation In} \xrightarrow{k_i} \text{r}^{\cdot} \xrightarrow{\text{RH}} \text{R}^{\cdot} \tag{i}$$

$$\text{Chain progagation} \quad \text{R}^{\cdot} \xrightarrow{\text{O}_2} \text{RO}_2^{\cdot} \xrightarrow{\text{RH}} \text{ROOH} + \text{R}^{\cdot} \tag{1, 2}$$

$$\text{Self-initiation} \quad \text{ROOH} \rightarrow \quad \text{Free radicals} \quad (\text{R}^{\cdot}) \tag{3}$$

$$\text{Chain termination} \quad \text{R}^{\cdot}\,(\text{RO}_2^{\cdot}) + \text{R}^{\cdot}\,(\text{RO}_2^{\cdot}) \rightarrow \quad \text{Molecular products} \tag{4—6}$$

With a practically constant rate of initiation, when $k_\text{i}[\text{In}] \gg k_3[\text{ROOH}]$, and a sufficiently high concentration of dissolved oxygen ($k_1[\text{O}_2] \gg k_2[\text{RH}]$) the rate of liquid-phase oxidation is described by a formula which for long chains becomes

$$W_{\text{O}_2} = a\,[\text{RH}]\,W_i^{1/2},$$

where W_i is the rate of initiation. The reason for the first order with respect to RH is that chain propagation is limited by the reaction $\text{RO}_2^{\cdot} + \text{RH}$, the order 0.5 with respect to the initiator is due to bimolecular (quadratic) chain termination, and the zero order with respect to oxygen is connected with preferential chain termination by reaction (6) between two peroxy-radicals. At low RH concentrations the oxidation chains are short, so that absorption of oxygen must be taken into account even in the act of initiation, and the rate of such absorption in the steady state is

$$W_{O_2} = 1/2W_i + a\,[\mathrm{RH}]\cdot W_i^{1/2}, \quad a = k_2\cdot k_6^{-1/2}.$$

This formula is valid for peroxide initiators, such as cumenyl, t-butyl, and benzoyl peroxides, whose decomposition yields alkoxy- or acyloxy-radicals that do not react with oxygen but attack the hydrocarbon. When initiators that generate alkyl radicals are used, such as azoisobutyronitrile, reaction of the initiator radical $r^{\cdot}$ with oxygen

$$\mathrm{r}^{\cdot} \xrightarrow{O_2} \mathrm{rO}_2^{\cdot} \xrightarrow{RH} \mathrm{R}^{\cdot} + \mathrm{rOOH}$$

must also be taken into account, so that

$$W_{O_2} = 3/2W_i + a\,[\mathrm{RH}]\cdot W_i^{1/2}\ .$$

With sufficiently long chains $W_{O_2} \simeq [\mathrm{RH}]W_i^{1/2}$: i.e. the reaction has the first order with respect to the hydrocarbon, and 0.5 with respect to the initiator, in agreement with experimental results (Table 1, cumene).

The equation of the above type for polymers PH in solution is[13]

$$W_{O_2} = 2W_i + a\,[\mathrm{PH}]\cdot W_i^{1/2}\ ,$$

For the oxidation of polystyrene in the presence of azoisobutyronitrile in benzene and in chlorobenzene a is respectively 3.6×10^{-4} and 5.0×10^{-4} $\mathrm{M^{-1/2}\ s^{-1/2}}$ at 333 K (activation energy $E = 74.2$ kJ mole^{-1}). The solvent may take part in the oxidation, which is apparently why the coefficient of W_i is 2, not $1\frac{1}{2}$, while the coefficient a has different values in the two solvents. Table 1 shows that the dependence of the rate of the initiated oxidation of polyethylene, polypropylene, and polystyrene on the initiator and polymer concentrations differs from the corresponding relation for a hydrocarbon [Eqns. (I) and (II), and data for cumene in Table 1]: the order with respect to the initiator always exceeds 0.5 and is close to unity. The first order has been established for polyethylene and polypropylene in chlorobenzene[14], which indicates the linear character of chain termination in the oxidation of polymers in solution. This is because the recombination of two peroxy-macroradicals $\mathrm{PO}_2^{\cdot}$ in solution takes place slowly owing to the slowness of the diffusion of one coiled macromolecule into another, so that chain termination results from reaction between a macroradical and molecules of low molecular weight arising from attack by radicals on solvent molecules.

Chlorobenzene is not absolutely inert[14], but slowly oxidises when cumenyl peroxide decomposes. Its rate of oxidation is described by Eqn. (I) with the coefficient $a = 3.85 \times 10^5 \exp(-68/RT)$. Oxidation is due to the ability of aromatic molecules to add radicals with subsequent generation of $\mathrm{HO}_2^{\cdot}$ and $\mathrm{HO}^{\cdot}$:

$$\mathrm{ROOR} \to 2\mathrm{RO}^{\cdot}$$

$$\mathrm{RO}^{\cdot} + \mathrm{ArH} \to \mathrm{RO\dot{A}rH}$$

$$\mathrm{RO\dot{A}rH} + \mathrm{O_2} \to \mathrm{ROAr} + \mathrm{HO}_2^{\cdot}$$

$$\mathrm{HO}_2^{\cdot} + \mathrm{ArH} \to \mathrm{ArOH} + \mathrm{HO}^{\cdot}$$

$$\mathrm{HO}^{\cdot} + \mathrm{ArH} \to \mathrm{HO\dot{A}rH}$$

$$\mathrm{HO\dot{A}rH} + \mathrm{O_2} \to \mathrm{ArOH} + \mathrm{HO}_2^{\cdot}\ .$$

When a polymer is oxidised in such a solvent, the $\mathrm{HO}_2^{\cdot}$ radicals diffuse rapidly and react with $\mathrm{PO}_2^{\cdot}$, thus effecting chain termination, the rate of which is directly proportional to the rate of reaction of $\mathrm{RO}^{\cdot}$ with the solvent, i.e. the rate of initiation W_i. The order of oxidation with respect to the polymer is always less than unity (Table 1); for polystyrene of number-average molecular mass 100 000 the kinetic order is zero[18].

When azoisobutyronitrile (AIBN) is used as initiator, it is improbable that 1-cyano-1-methylethylperoxy-radicals formed from the initiator in the presence of oxygen will attack the solvent (benzene) molecules. At low polymer (PH) concentrations in such systems ($\mathrm{ArH{-}[CN.C(CH_3)_2.N{:}]_2{-}O_2{-}PH}$) a peroxy-radical of the initiator apparently reacts with the peroxy-macroradical. At sufficiently high PH concentrations $\mathrm{HO}_2^{\cdot}$ radicals, formed after $\mathrm{RO}^{\cdot}$ and $\mathrm{HO}^{\cdot}$ radicals appearing in the system have interacted with the solvent, may be involved in termination.

The primary reason for the diminished order with respect to the oxidisable compound on passing from a hydrocarbon to a polymer is that oxidation in the latter takes place predominantly within each coiled macromole-

Table 1. Kinetics of the oxidation of polymers in solution (I = light intensity).

Polymer	Solvent	Initiator	T, K	[PH] or [RH], M	Rate of oxidation	Chain length	Ref.
Polyethylene	C_6H_5Cl	cumenyl peroxide	391	0.1—3	$[\mathrm{In}]\cdot[\mathrm{PH}]^{0.37}$	1—4	14
Isotactic	C_6H_5Cl	cumenyl peroxide	384	0.1—1.3	$[\mathrm{In}]\cdot[\mathrm{PH}]^{0.55}$	2—9	14
polypropylene	C_6H_6	t-butyl peroxide	373—403	0.8—4.0	$[\mathrm{In}]^{0.85}\cdot[\mathrm{PH}]^{0.73}$	7—30	15
Atactic	$C_6H_3Cl_3$	AIBN	353—373	2.05—0.25	$[\mathrm{In}]^{0.85}\cdot[\mathrm{PH}]^{0.37}$	—	16
polypropylene	$C_6H_3Cl_3$	AIBN	353—373	0.25—1.50	$[\mathrm{In}]^{0.85}\cdot[\mathrm{PH}]^{0.12}$	—	16
Polystyrene	C_6H_5Cl	AIBN	333	0.05—0.88	$[\mathrm{In}]^{0.75}\cdot[\mathrm{PH}]^{0.34}$	1	17
$\overline{M}_n = 10^4$	C_6H_5Cl	AIBN + $h\nu$	298	0.1—1.0	$[\mathrm{In}]^{0.85}\cdot I^{0.92}\cdot[\mathrm{PH}]^{0.62}$	2.4	18
$\overline{M}_n = 10^5$	C_6H_5Cl	AIBN + $h\nu$	298	0.1—1.0	$[\mathrm{In}]^{0.94}\cdot I^{0.98}\cdot[\mathrm{PH}]^{0}$	1.5	18
Cumene	C_6H_5Cl	AIBN + $h\nu$	298	0.1—1.0	$[\mathrm{In}]^{0.51}\cdot I^{0.52}\cdot[\mathrm{RH}]^{0.98}$	23	18
2,4-Diphethylpentane	C_6H_5Cl	AIBN + $h\nu$	298	0.1—1.0	$[\mathrm{In}]^{0.68}\cdot I^{0.65}\cdot[\mathrm{RH}]^{0.81}$	4	18

*AIBN = azoisobutyronitrile.

cule. As soon as all the initiator radicals have reacted with the polymer to form P$^\cdot$ radicals (for which a minimum concentration $[PH]_{min}$ is required), further oxidation as a sequence of steps (1) and (2) takes place within a single macromolecule, resulting in a lower order of oxidation with respect to the polymer. Comparison of the photoinitiated oxidation of cumene, 2,4-diphenylpentane, and polystyrene (Table 1) leads to the same conclusion: whereas for cumene the kinetic order with respect to PH is unity, diphenylpentane undergoes appreciable intramolecular isomerisation of $RO_2^\cdot$ and the order with respect to RH is 0.8, while in polystyrene having $\overline{M}_n = 10^4$ the order with respect to PH is 0.6.[18]

Convincing evidence that in solution chain oxidation develops within a single macromolecule is provided by a comparison[14] of the rates of initiated oxidation of the n-decane–2,2,4-trimethylpentane and polyethylene–polypropylene systems. In the former case the rate of oxidation passes first through a maximum and then through a minimum with change in composition of the hydrocarbon mixture, such variation being due to the different activities of secondary and tertiary peroxy-radicals in chain propagation and termination[19]. In the latter case the rate of oxidation varies linearly with the composition of the polymer mixture, which indicates the absence of cross propagation and termination, possible only when the chain oxidation develops inside each separate coiled molecule.

Thus the kinetics of the oxidation of polymers in solution differs significantly from that of the oxidation of hydrocarbons in the participation of simple initiator or solvent radicals in chain termination, while chain oxidation develops within each macromolecule. Both circumstances result in slower oxidation of a polymer than of the model hydrocarbon.

III. REACTIVITY OF POLYMERS AND MODEL HYDROCARBONS

Since polymers and hydrocarbons differ in the kinetics of their initiated oxidation (Table 1), comparison of their rates of oxidation under similar conditions will not give a correct idea of the reactivities of carbon–hydrogen bonds in polymers and in model hydrocarbons. An example is provided by data on the oxidation of polypropylene and 2,2,4-trimethylpentane (RH) in the presence of 0.01 M azocyclohexanecarbonitrile in chlorobenzene at 363 K:[20] for the hydrocarbon the ratio $W_{O_2}/[RH]W_i^{1/2} = 4.1 \times 10^{-5}$ $M^{-1/2}$ $s^{-1/2}$, whereas the corresponding ratio for the polymer (per gram-equivalent of the monomer unit) is some hundredfold greater, i.e. 1.5×10^{-3}. We shall see below that the reactivity of a tertiary carbon–hydrogen bond in polypropylene is closely similar to that for 2,2,4-trimethylpentane.

During recent years rate constants have been measured for the reactions of peroxy- and alkoxy-radicals with carbon–hydrogen bonds in polymers and in model hydrocarbons. Cumene (RH) and polyethylene (PH) were oxidised together, and the quantities of ROOH and POOH were determined[21]. The ratio [POOH]/[ROOH] gave the ratio of the rate constants k_2^{PH}/k_2^{RH}, and k_2 was calculated for the reaction of the cumenylperoxy-radical with a carbon–hydrogen bond in polyethylene in solution. The rate of oxidation of polypropylene was measured in the presence of an initiator and t-butyl hydroperoxide[20], reaction with which caused rapid exchange of $PO_2^\cdot$ by $(CH_3)_3COO^\cdot$ radicals, so that the rate of oxidation of polypropylene was

$$W_{O_2} = (k_2/\sqrt{k_6}) \cdot [PH] \cdot [(CH_3)_3COO^\cdot]$$

from which k_2 could be calculated when k_6 was known. Peroxy-radicals of polystyrene (ps) recombine rapidly, so that its addition to cumene tended to inhibit oxidation of the latter[22]. The ratio k_2^{ps}/k_2^{RH} was found from the dependence of W_{O_2} on the concentration of polystyrene, and hence k_2^{ps} was calculated[22]. Rate constants for the abstraction of hydrogen from PH and RH by t-butoxy-radicals were measured by a method of competing reactions[23]. The results of these investigations are summarised in Table 2.

A comparison of polyethylene and polypropylene with model hydrocarbons shows that carbon–hydrogen bonds in a polymer and in the corresponding model have similar reactivities (differing not more than twofold, within the limits of error in the calculation of absolute rate constants). However, a marked (tenfold) difference in reactivity is observed between polystyrene and the model hydrocarbon cumene[22,25]. The most probable reason why a carbon–hydrogen bond is attacked more slowly in polystyrene when in cumene is steric hindrance by neighbouring phenyl rings. Detachment of hydrogen from such a

Table 2. Rate constants k* for reactions of peroxy- and alkoxy-radicals with C–H bonds in polymers and model hydrocarbons.

Oxidisable compound	Radical	Solvent	T, K	k, M^{-1} s^{-1}	Ref.
Polyethylene	$C_6H_5C(CH_3)_2OO^\cdot$	$C_6H_5CH(CH_3)_2$	388	0,12	21
n-Decane	$C_6H_5C(CH_3)_2OO^\cdot$	C_6H_5Cl	388	$10^{8,68}\exp(-73/RT)=0,063$	4
Polypropylene	$(CH_3)_3COO^\cdot$	C_6H_5Cl	363	0,98	20
2,6,10,14-Tetramethylpentadecane	$(CH_3)_3COO^\cdot$	C_6H_5Cl	363	0,58	20
Isopentane	$(CH_3)_2(C_2H_5)COO^\cdot$	$(CH_3)_2CHC_2H_5$	363	$10^{8,3}\exp(-66/RT)=0,35$	24
Polypropylene	$C_{10}H_{11}OO^\cdot$	C_6H_5Cl	363	3,3	20
2,6,10,14-Tetramethylpentadecane	$C_{10}H_{11}OO^\cdot$	C_6H_5Cl	363	2,1	20
Polystyrene	$C_6H_5C(CH_3)_2OO^\cdot$	$C_6H_5CH(CH_3)_2$	353	$10^{9,7}\exp(-72/RT)=0,10$	22
Cumene	$C_6H_5C(CH_3)_2OO^\cdot$	$C_6H_5CH(CH_3)_2$	353	$10^{6,7}\exp(-41/RT)=4,2$	25
Polystyrene	$(CH_3)_3CO^\cdot$	C_6H_6	313	26*	23
2,4-Dimethylpentane	$(CH_3)_3CO^\cdot$	C_6H_6	313	125*	23
Cumene	$(CH_3)_3CO^\cdot$	C_6H_6	313	1020*	23
Polystyrene	$(CH_3)_3CO^\cdot$	C_6H_6	318	26*	26
Cumene	$(CH_3)_3CO^\cdot$	C_6H_6	318	1600*	26
Polypropylene	$(CH_3)_3CO^\cdot$	C_6H_6	318	137*	26
2,2,4-Trimethylpentane	$(CH_3)_3CO^\cdot$	C_6H_6	318	300*	26

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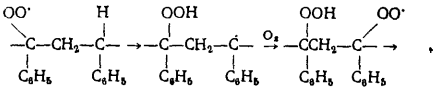
*Values of k calculated from k/k_d ratios, where $k_d = 10^{13.5}\exp(-69/RT)$ s^{-1} is the decomposition rate constant of the t-butoxy-radical (it has the values 100 and 140 s^{-1} at 313 and 318 K respectively)[27].

bond in cumene produces a cumenyl radical, which is stabilised by interaction of the p orbital of the unpaired electron with π orbitals of the phenyl ring. In polystyrene such stabilisation, which requires coplanarity of the phenyl ring and adjacent carbon–carbon bonds, is made difficult by neighbouring phenyl rings, which prevent such coplanarity. This explanation is supported by a comparison of the rate constants for reactions of the t-butoxy-radical with cumene, 2,4-diphenylpentane, and polystyrene (Table 2): rates of attack on a carbon–hydrogen bond are 5 times as rapid in diphenylpentane as in polystyrene, and ~10 times as rapid in cumene as in diphenylpentane. It is also interesting that the rate constant for chain propagation in polystyrene is $10^6 \exp(-33/RT) = 12.5\ M^{-1}\ s^{-1}$, which is hundredfold the rate constant for reaction of the cumenylperoxy-radical with a carbon–hydrogen bond in polystyrene[13]. If no experimental error is involved in the measurement of k_6 (which together with the ratio $k_2/k_6^{1/2}$ was used to calculate k_2), this can be explained by intramolecular chain propagation:



$$-\underset{C_6H_5}{\overset{OO^\cdot}{C}}-CH_2-\underset{C_6H_5}{\overset{H}{C}}- \rightarrow -\underset{C_6H_5}{\overset{OOH}{C}}-CH_2-\underset{C_6H_5}{\dot{C}}- \xrightarrow{O_2} -\underset{C_6H_5}{\overset{OOH}{C}}CH_2-\underset{C_6H_5}{\overset{OO^\cdot}{C}}- \rightarrow\ ,$$

Thus carbon–hydrogen bonds in a polymer exhibit the same reactivity towards free radicals as do those in a model hydrocarbon, provided that neighbouring groups do not create steric hindrance, as occurs in polystyrene.

IV. SIMILARITY OF THE MECHANISMS OF OXIDATION OF LIQUID HYDROCARBONS AND SOLID POLYMERS

Solid carbon-chain polymers, like liquid hydrocarbons, are oxidised by a chain mechanism involving alkyl and peroxy-radicals. This is demonstrated by investigations on the initiated oxidation of polymers, in which $W_{O_2} \gg W_i$ at not very high rates of initiation, and the chain length usually varies over the range $\nu = 5-200$ monomer units. Rate constants for initiation and for the decomposition of several initiators in polymers are given in Table 3. The liquid-phase chain oxidation of hydrocarbons involves alkyl and peroxy-radicals, the latter recorded by electron spin resonance[3]. The oxidation of solid polymers also is accompanied by formation of peroxy-radicals, detected by e.s.r. both in low-temperature radiation-chemical oxidation[43] and in oxidation in the presence of initiators at ~373 K (see Section VI).

During recent years important data on the mechanism of the oxidation of solid carbon-chain polymers have been obtained by the use of initiated oxidation, in which a known fixed rate of generation of free radicals enables the dependence of rate of oxidation on reactant concentrations and on rate of generation to be examined, the length of the chain to be calculated, and a quantitative measure of the oxidisability of a substance to be obtained as the overall constant in the formula

$$W_{O_2} = \text{const}\,[RH]^{n_1}\cdot[O_2]^{n_2}\cdot W_i^{n_3}\ .$$

The rate of the initiated oxidation of solid polymers, like the liquid-phase oxidation of hydrocarbons, is proportional to $W_i^{1/2}$ (Table 4). Hence in both solid and liquid phases chain termination results from the encounter and loss of two active centres (bimolecularly). As in the liquid phase, the rate of oxidation is independent of the partial pressure of oxygen when the latter is "high" (~1 atm).[38]

It is interesting to compare the rates of oxidation of polymers and model hydrocarbons. For polyethylene the ratio $W_{O_2}/W_i^{1/2} = 0.9 \times 10^{-5}$ per methylene group at 373 K (Table 4 [40]); but for a methylene group in cyclohexane[44] $k_2k_6^{-1/2} = 7.6 \times 10^{-5}$, an almost tenfold difference. On the other hand, polypropylene and isopentane are closely similar in oxidisability: $W_{O_2}/W_i^{1/2} = 6.4 \times 10^{-4}$ for one monomeric group in the polymer (Table 4 [38]) and $k_2k_6^{-1/2} = 4.5 \times 10^{-4}$ for isopentane (373 K).[24] The fact that, in the absence of an inhibitor, the rate of oxidation of a polymer in the solid phase is directly proportional to $W_i^{1/2}$ proves that chain termination always occurs by a bimolecular

Table 3. Decomposition rate constants and efficiency of initiators in solid polymers ($k_i = 2ek$).

Initiator	Polymer	T, K	k or k_i, s^{-1}	e	Ref.
AIBN	polystyrene	353	—	0.05	28
AIBN	polystyrene	333—353	$k_i = 5.5\cdot10^{13}\exp(-128/RT)$	—	29
AIBN	polyethylene	335	$k_i = 0.8\cdot10^{-7}$	0.005	30
AIBN	polyethylene	343	$k_i = 0.3\cdot10^{-6}$	0.006	30
AIBN	polyethylene	363	$k_i = 9.3\cdot10^{-6}$	0.02	30
AIBN	polyethylene	365,5	$k_i = 4.7\cdot10^{-5}$	0.07	30
AIBN	polypropylene	333—358	$k_i = 5.1\cdot10^{17}\exp(-154/RT)$	0.05*	31
Benzoyl peroxide	polystyrene	329—355	$k = 2.6\cdot10^{17}\exp(-150/RT)$	—	32
Benzoyl peroxide	polystyrene	355—371,5	$k = 6.7\cdot10^{13}\exp(-126/RT)$	—	32
Benzoyl peroxide	polyethylene	365	$k_i = 4.5\cdot10^{-5}$	—	34
Benzoyl peroxide	polypropylene	365	$k_i = 4.5\cdot10^{-5}$	—	34
Benzoyl peroxide	polypropylene	360	$k_i = 5.9\cdot10^{-5}$	—	33
Benzoyl peroxide	polypropylene	344—365	$k = 8.4\cdot10^{13}\exp(-124/RT)$	0.14—0.62	35
Benzoyl peroxide	polypropylene	340—360	$k = 4.5\cdot10^{13}\exp(-124/RT)$	—	36
Benzoyl peroxide	polybut-1-ene	349—383	$k = 8.4\cdot10^{13}\exp(-124/RT)$	0.018—0.59	35
Benzoyl peroxide	poly-4-methylpent-1-ene	344—365	$k = 7.0\cdot10^{13}\exp(-122/RT)$	0.012—0.05	35
Benzoyl peroxide	poly(ethyl acrylate)	358—383	$k = 8.0\cdot10^{13}\exp(-123/RT)$	—	37
Benzoyl peroxide	poly(vinyl chloride)	337—350	$k = 1.55\cdot10^{20}\exp(-170/RT)$	—	32
Benzoyl peroxide	poly(vinyl chloride)	350—363	$k = 6.9\cdot10^{18}\exp(-162/RT)$	—	32
Benzoyl peroxide	poly(vinyl chloride)	363—371,5	$k = 1.2\cdot10^{15}\exp(-136/RT)$	—	32
Cumenyl peroxide	polyethylene	382—391	$k_i = 8.5\cdot10^{15}\exp(-157/RT)$	—	38
Cumenyl peroxide	polypropylene	373—395	$k_i = 1.1\cdot10^{13}\exp(-135/RT)$	—	34
Cumenyl peroxide	polypropylene	388	$k_i = 8.1\cdot10^{-6}$	—	33
Di-t-butyl peroxalate	polypropylene	298	—	0.014	39
Di-t-butyl peroxalate	polypropylene	308	—	0.033	39
Di-t-butyl peroxalate	polypropylene	318	—	0.061	39
Di-t-butyl peroxalate	polypropylene	328	—	0.15	39
Peroxide of plamitic acid	polystyrene	333—353	$k_i = 2.1\cdot10^{14}\exp(-127/RT)$	—	29
Peroxide of lauric acid	polystyrene	353	—	0 33	28
Peroxide of lauric acid	polyethylene	353	—	0.46	28

*At 353 K.

reaction. Therefore all schemes of uninhibited oxidation involving any linear mechanism of chain termination in the polymer[9,45-47] should be reconsidered as inconsistent with experiment.

Table 4. Values of $W_{O_2}/W_i^{1/2}$ for polymers in the solid phase.

Polymer	Initiator	T, K	$W_{O_2}\,W_i^{-1/2}$, mole$^{1/2}$ kg$^{-1/2}$ s$^{-1/2}$	Ref.
Polyethylene*	cumenyl peroxide	389—402	$1.6\cdot10^{10}\exp(-88/RT)$	40
Polyethylene*	$\gamma(^{60}Co)$	318	$1.25\cdot10^{-3}$	42
Polypropylene, isotactic*	benzoyl peroxide	353—378	$1.4\cdot10^{6}\exp(-56/RT)$	38
Polypropylene, atactic	$\gamma(^{60}Co)$	295	$4.0\cdot10^{-3}$	41
Polypropylene, atactic	$\gamma(^{60}Co)$	318	$1.2\cdot10^{-2}$	41
Polypropylene, isotactic*	benzoyl peroxide	344—378	$73\exp(-26/RT)$	35
Polypropylene, amorphous	benzoyl peroxide	358—378	$8.5\cdot10^{8}\exp(-71/RT)$	37
Polypropylene, isotactic*	azoisobutyronitrile, POOH	317—365	$4.0\cdot10^{2}\exp(-27.8/RT)$	31
Polybut-1-ene	benzoyl peroxide	363	$2.1\cdot10^{-2}$	35
Polybut-1-ene	benzoyl peroxide	378	$5.4\cdot10^{-2}$	35
Copolymer*, 37**	$\gamma(^{60}Co)$	318	$5.7\cdot10^{-3}$	42
Copolymer*, 73**	$\gamma(^{60}Co)$	318	$1.6\cdot10^{-3}$	42
Copolymer, 65**	benzoyl peroxide	358—378	$3.8\cdot10^{8}\exp(-71/RT)$	37
Copolymer, 87**	benzoyl peroxide	353—369	$2.7\cdot10^{5}\exp(-54/RT)$	38
Copolymer, 96**	cumenyl peroxide	388,5	$1.6\cdot10^{-2}$	38
Copolymer, 98**	cumenyl peroxide	382—400	$1.0\cdot10^{9}\exp(-81/RT)$	38
Poly(ethyl acrylate)	benzoyl peroxide	358—378	$7.6\cdot10^{5}\exp(-54/RT)$	37

*Calculated for the amorphous phase: i.e. multiplied by $\alpha^{1/2}$, where α is the fraction of the amorphous phase.
**Percentages of ethylene in its copolymers with propene.

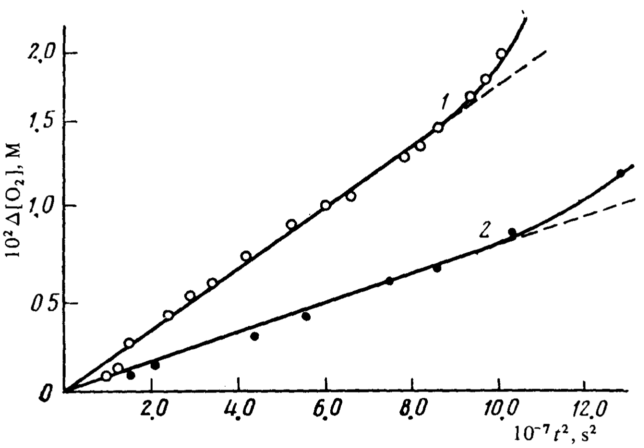


Figure 1. Kinetic curves for the autoxidation of polypropylene at 387 K under different oxygen pressures: 1) 1 atm; 2) 0.6 atm.

The uninitiated oxidation (autoxidation) of hydrocarbons and polymers is characterised by autocatalysis[3,7,48] due to the accumulation of hydroperoxide, an intermediate product that breaks down into free radicals. Both in liquid and in solid phases, therefore, oxidation is a self-initiated chain reaction (a chain reaction with degenerate branching of the chains). Since chains are terminated by a bimolecular reaction, the rate of autoxidation of a hydrocarbon is described by the equation[4]

$$d\Delta[O_2]/dt \cong k_2 k_6^{-1/2}\cdot[RH]\cdot(k_3[ROOH])^{1/2}$$

or

$$\Delta[O_2] \cong \frac{1}{4}(k_2 k_3^{1/2} k_6^{-1/2}\cdot[RH])^2\cdot t^2$$

provided that the rate of generation of chains is small ($W_{i0} \ll k_3[ROOH]$ almost throughout the experiment) and the whole of the oxygen absorbed is converted into hydroperoxide. The parabolic kinetic law, $\Delta[O_2] \propto t^2$ is due to the fact that self-initiation is a first-order reaction, whereas chain termination has a bimolecular mechanism. Both factors apply also to the oxidation of polymers in the solid phase, which therefore is also described (Fig. 1) by the kinetic law

$$\Delta[O_2]^{1/2} = b\cdot t\ .$$

In view of the above considerations use of the kinetic law $\Delta[O_2] \propto e^{\varphi t}$ (e.g. Ref. 48) for the uninhibited oxidation of solid polymers is evidently incorrect.

Thus oxidation both of liquid hydrocarbons and of solid carbon-chain polymers is a self-initiated chain reaction involving alkyl and peroxy-radicals with bimolecular chain termination. Within the framework of such a definition we can speak of a single radical–chain mechanism for the oxidation of liquid hydrocarbons and solid polymers. It is interesting that the gas-phase oxidation of hydrocarbons falls outside the scope of such a definition and has a different mechanism[49], in which not only $R^{\bullet}$ and $RO_2^{\bullet}$ but also alkoxy-radicals play an important part in chain propagation, and the reaction between two $RO_2^{\bullet}$ radicals involves not termination but propagation: $2RO_2^{\bullet} \rightarrow 2RO^{\bullet} + O_2$.

V. PRIMARY RADICAL REACTION IN A POLYMER MATRIX

In a condensed phase (liquid or solid) a bimolecular reaction between freely diffusing reactants takes place in two stages, with diffusion of two particles into the same cage followed by their collision and reaction in the cage[50]:

$$A + B \underset{k'_D}{\overset{k_D}{\rightleftarrows}} A\cdot B \xrightarrow{k} \text{Products}\ .$$

Depending on the relation between k and k'_D reactions are divided into slow ($k \ll k'_D$) and rapid or diffusion-controlled ($k \geqslant k'_D$). In a solution the cage walls consist of molecules undergoing quite rapid rotation (10^9–10^{11} s^{-1}) and translation (a molecular diameter in 10^{-9}–10^{-10} s). In the liquid phase, therefore, the form of the cage changes rapidly, and in the absence of orientational interactions between the molecules the cage walls can be regarded as an isotropic viscous medium surrounding the pair of reacting particles. In such a cage it may be expected that all mutual orientations of the particles will be equivalent, and that the steric factor for the bimolecular reaction will be closely similar to that for a gas-phase reaction.

An amorphous polymer phase resembles a liquid with regard to molecular motion, but displacements and rotations of segments and molecules are comparatively slow owing to the great length of the macromolecular chains and the large energy of intermolecular interaction of the chains. As a consequence, the shape of the cage formed by segments of the macromolecule changes slowly in the amorphous phase when compared with the liquid, the relaxation time of the form of the cage in the polymer is long, and the cage can be regarded as a kind of "bag" with rigid walls surrounding the pair of reactant particles[51]. In such a "rigid" cage by no means all the mutual orientations of the reactant particles are energetically equivalent. If an orientation required the consumption of energy is necessary for a primary step, the steric factor P for such a reaction will be smaller in the polymer than in the liquid phase, and will depend on the temperature: $P = P_0 e^{-E_{or}/RT}$, where E_{or} is the activation energy of orientation of the particles due to the energy consumed in overcoming the action of the rigid polymer matrix, i.e. in orienting the particles. Such a model of a rigid cage (a cage with slow relaxation of its shape and size) leads to the qualitative conclusions outlined below[51].

1. The rate constant for species requires a precise orientation before they can react should be smaller in a solid polymer matrix than in the liquid phase. This conclusion is supported by comparison of the rate of such reactions as the oxidation of dinaphthyl-*p*-phenylenediamine by a hydroperoxide (k_*/k_{sd} = 7.4 in polypropylene at 373 K [52]), the reaction of tri-t-butylphenoxyl with POOH (43 in polypropylene at 295 K [53]), and the action of the nitroxyl radical on 2,6-di-t-butylphenol[54] (14 in polyethylene at 313 K).
2. The activation energy of a bimolecular reaction should be greater in the solid phase than in solution. This conclusion is consistent with data on termination reactions: for the reaction of 2,4,6-tri-t-butylphenoxyl with POOH in benzene and in polypropylene the activation energy is respectively 45.5 and 67 kJ mole^{-1};[53] the corresponding values for the action of the nitroxyl radical on 2,6-di-t-butylphenol are 42 and 75 kJ mole^{-1}.[54]
3. Introduction of a simple compound into a polymer, by increasing the molecular mobility and making the cage more elastic (shortening the relaxation time of its shape), should accelerate a bimolecular reaction. Benzene actually has such an effect on the above two reactions[53,54].
4. Since both the mutual orientation of species and the rotation of a species in a cage involve overcoming forces of repulsion due to "neighbours", a parallelism can be expected in the variation of the rate constant of a bimolecular reaction and the frequency of rotation of a species, e.g. a stable nitroxyl radical, with change in the polymer matrix. Such parallelism has been demonstrated[12,53,54]. It is interesting that the activation energy of rotation E_ν and the difference in activation energy of the reaction in solid and liquid phases are then closely similar (respectively 40 and 33 kJ mole^{-1}).[53,54]
5. Rise in temperature is accompanied by an increase in molecular mobility in the polymer, a shortening of the relaxation time of the cage shape, and an increase in the elasticity of the cage. As a consequence, the orientation of the reactant species necessary for the primary step is more easily attained, and E_{or} is lowered. Thus, since in the solid phase the total activation energy $E_\Sigma = E_{or} + E$, while E_{or} decreases with rise in temperature, it follows that E_Σ is an effective quantity that decreases with rise in temperature.

Termination in the solid phase may also be retarded by a possible delay between the abstraction of hydrogen and rehybridisation of *p* orbitals of the carbon atom under attack[55]. However, the difference between the rate constants for abstraction of a hydrogen atom by peroxy-radicals in solution and in the solid phase (see below) is small, so that delay in rehybridisation is not evident here. At the given temperatures the molecular mobility of the macromolecular segments is apparently sufficient to ensure rehybridisation of orbitals immediately on accomplishment of the primary step.

Another substantial difference between a solid polymer and a liquid is the inhomogeneity of a polymer as a medium. Firstly, a polymer (polyethylene, isotactic polypropylene, ethylene–propylene copolymers, etc.) comprises crystalline and amorphous phases. If the former is more densely packed than the latter, dissolution and interaction of the reactants will occur predominantly in the amorphous phase. Electron spin resonance has shown[53] that nitroxyl radicals dissolve only in the amorphous phase. Secondly, the amorphous phase of a polymer is itself non-uniform, consisting of a series of zones differing in molecular mobility. This leads to so called polychromatic kinetics both of radical reactions and of physical processes, e.g. diffusion in a polymer[56–60]. With rise in temperature the polychromatism disappears, apparently because of increasing mobility of the molecules and more rapid migration of density fluctuations along the polymer (the amorphous phase approaches a liquid in molecular mobility). Thus a polymer differs from a liquid as a medium in its more rigid cage structure (the shape of the cage changes slowly) and in inhomogeneity. These two features affect the kinetics of radical reactions in a polymer.

Table 5. Specific rates of generation of chains in polymers and model hydrocarbons.

Oxidisable compound	T, K	k_{i0}, M^{-1} s^{-1}	E_{i0}, kJ mole^{-1}	Ref.
Polypropylene (solid)*	405	$8.5 \cdot 10^{-5}$	92	63
Polypropylene (solution)	403	$2.9 \cdot 10^{-6}$	98	63
Isopentane	410	$1.3 \cdot 10^{-8}$	158	64
Low-pressure polyethylene* (solid)	404	$1.3 \cdot 10^{-5}$	117	63
High-pressure polyethylene* (solid)	377	$2.5 \cdot 10^{-6}$	146	63
n-Heptane	406	$2.3 \cdot 10^{-9}$	181	65

*Here calculation of k_{i0} per monomer unit was based on the amorphous phase.

VI. CHAIN GENERATION AND PROPAGATION

Generation of Chains

In hydrocarbons undergoing oxidation, chains are generated by reactions involving oxygen. Most often generation occurs by the bimolecular reaction[61]

$$RH + O_2 \rightarrow R^{\cdot} + HO_2^{\cdot},$$

whose activation energy approximates to its endothermicity. In compounds having weak carbon–hydrogen bonds (bonding energy < 330 kJ mole^{-1}) chains are generated mainly by the termolecular reaction[3]

$$2RH + O_2 \rightarrow 2R^{\cdot} + H_2O_2 \ .$$

The reaction

$$C_6H_5CH_2CH_3 + 2O_2 \rightarrow C_6H_5CH\dot{C}H_2 + 2HO_2^{\cdot}$$

has been demonstrated[62] for ethylbenzene.

In the only study of chain generation in polymers (polyethylene, polypropylene)[63] the rate of formation of radicals was measured by an inhibitor method from the consumption of 1-naphthol and *NN'*-dinaphth-2-yl-*p*-phenylenediamine. Chain generation was shown to involve oxygen, which in effect dissolves only in the amorphous phase, so that generation was concentrated therein. In the solid phase the specific rate of chain generation $k_{i0} = W_{i0}/\alpha[O_2][PH]$ (in which α is the fraction of the amorphous phase) is significantly higher than in solution (Table 4) and higher than in model hydrocarbons by several orders of magnitude. In a polymer chains are probably generated by reaction between oxygen and residues of the catalyst. The higher specific rate in the solid phase than in solution (Table 5) can be explained by the presence of "weak" carbon–hydrogen bonds in deformed segments of the macromolecular chains. A relatively high rate in polymers must be taken into account in the use of inhibitors for the stabilisation of polymers and in interpretation of the results of experiments with inhibitors. In particular, the high value of W_{i0} in polypropylene casts doubt on the legitimacy of applying the theory of critical phenomena in inhibited oxidation, since quite a high k_3/W_{i0} ratio is then necessary[66].

Reaction $P^{\cdot} + O_2 \rightarrow PO_2^{\cdot}$

The addition of oxygen to alkyl radicals is very rapid, its rate being limited by diffusion of the gas into the polymer. For example, the rate constant for addition of oxygen to the methyl radical in water is 5×10^9 M^{-1} s^{-1}.[19] The kinetics of the $P^{\cdot} + O_2$ reaction in polymers has been studied by low-temperature e.s.r. with radiation-chemical generation of $P^{\cdot}$ (Table 6). Owing to the non-uniformity of the polymer and differences in the diffusion coefficients of oxygen in different zones, the reaction with alkyl radicals is described by a polychromatic kinetic equation with an activation-energy particle distribution (every zone has its own activation energy for the diffusion of oxygen). Table 6 gives values of $E_{\min}$ and $E_{\max}$ calculated for a linear energy distribution of $P^{\cdot}$. Earlier measurements of k_1 and E_1 have been given in a review[5].

Table 6. Rate constants of the reaction $P^{\cdot} + O_2$ in polymers.

Polymer	T, K	E, kJ mole^{-1}	lg (A, M^{-1} s^{-1})	Ref.
Isotactic polypropylene, powder	373	—	6.4*	34
Isotactic polypropylene, film	100—140	$E_{\min}$=33; $E_{\max}$=44	14	67
Atactic polypropylene, film	100—140	$E_{\min}$=19; $E_{\max}$=25	9	67
Polystyrene	90—120	$E_{\min}$=29; $E_{\max}$=35	13	68
Polystyrene	94—140	$E_{\min}$=22.5; $E_{\max}$=27	12	69

*Value of lg (k, M^{-1} s^{-1}).

Since diffusion in a polymer is due to segmental mobility, while rise in temperature produces an abrupt release of degrees of freedom, it follows that $E_{\text{diff}} = E_1$ changes from one temperature range to another. Therefore the extrapolation of k_1 to the comparatively high oxidation temperatures will give incorrect estimates. The only estimate of k_1 for 373 K (oxidation temperature) was based[34] on the dependence of rate of oxidation on partial pressure of oxygen (the ratio $k_1/k_4^{1/2}$ was found) with the value $k_4 = 2.7 \times 10^6$ M^{-1} s^{-1} measured by e.s.r.

The Reaction $PO_2^{\cdot} + PH \rightarrow POOH + P^{\cdot}$

Reaction rate constants for peroxy-radicals in polymers have been studied by electron spin resonance—at low temperatures (below room temperature) from the kinetics of the disappearance of $PO_2^{\cdot}$, and under oxidation conditions from the rate of oxidation at the steady-state concentration of peroxy-radicals ($k_2 = W_{O_2}/[PO_2^{\cdot}]$)—and the results are listed in Table 7. The activation energy for the $PO^{\cdot} + PH$ in polyethylene[70] seems to be greatly underestimated. It must be expected that in the solid phase $E > E_{\text{liq}}$. For the reaction of cumenylperoxy-radicals with n-decane $E_2 = 73$ kJ mole^{-1} (Table 2), whereas in polyethylene $E_2 = 39$ kJ mole^{-1} (Table 7). Furthermore, a carbon–hydrogen bond in polyethylene is more stable than a tertiary bond in polypropylene, so that E_2 should be higher in the former than in the latter polymer, whereas the opposite situation has been observed[70]. On the other hand, E_2 is higher in deuterated than in ordinary polyethylene, which indicates the loss of $PO_2^{\cdot}$ by reaction with a C–H (C–D) bond.

Table 7. Rate constants of $PO_2^{\cdot} + PH$ reactions in solid polymers calculated per monomer unit.

Polymer	Initiation	T, K	A, M^{-1} s^{-1}	E, kJ mole^{-1}	Ref.
Polyethylene	γ (Co^{60})	230—270	$8.4 \cdot 10^2$	39	70
Deuterated polyethylene	γ (Co^{60})	270—300	$9.6 \cdot 10^2$	43	70
Isotactic polypropylene	POOH	383—413	$3.0 \cdot 10^5$	38	71
Isotactic polypropylene	AIBN, POOH	317—365	$9.6 \cdot 10^{11}$	87.8	31
Amorphous polypropylene	benzoyl peroxide	363—378	$1.6 \cdot 10^7$	51	35
Amorphous polypropylene	di-t-butyl peroxolate	318	$7.7 \cdot 10^{-3}$***		42
Isotactic polypropylene	γ (Co^{60})	270—310	$1.1 \cdot 10^4$	53	70
Isotactic deuterate polypropylene	γ (Co^{60})	270—310	$1.5 \cdot 10^4$	58	70
Amorphous polystyrene	mechanochemical	210—293	$3.5 \cdot 10^8$*	43*	72
Amorphous polystyrene	mechanochemical	210—293	$1.3 \cdot 10^{12}$***	88**	72
Poly(methyl methacrylate)	mechanochemical	250—360	$1.0 \cdot 10^6$	50	73

*For maximum value of k_2.

**For minimum value of k_2.

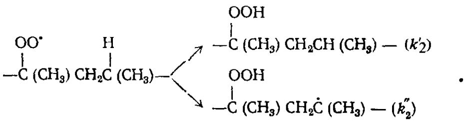
***Value of k.

Values of k_2 must be expected to be smaller in the solid phase than in solution (see above and Tables 2 and 7). In solution at 388 K the cumenylperoxy-radical attacks a carbon–hydrogen bond in polyethylene with $k_2 = 0.12$ M^{-1} s^{-1}. In the solid phase extrapolation of k_2 to 388 K gives 0.0012 M^{-1} s^{-1} per bond (Table 7): i.e. in the solid phase abstraction of a hydrogen atom by the peroxy-radical is slower by a factor of 100.

We reach a similar conclusion if we compare $k_2 = 0.05$ M^{-1} s^{-1} in poly(methyl methacrylate) [monomeric unit $-CH_2\overset{|}{C}(CH_3)COOCH_3$] at 360 K with the rate constant $k_2 = 24$ M^{-1} s^{-1} for reaction of the cumenylperoxy-radical with methyl propionate at the same temperature[4]. At first glance a different conclusion is reached from a comparison of k_2 for polypropylene in solution and in the solid phase: the t-butylperoxy-radical attacks a tertiary carbon–hydrogen bond in polypropylene with $k_2 = 0.98$ M^{-1} s^{-1} at 338 K (Table 2), whereas in solid atactic polypropylene $k_2 = 0.7$ M^{-1} s^{-1} (Table 7).[35] However, these constants represent different processes. In the oxidation of polypropylene in the presence of a hydroperoxide in solution k_2 relates to the reaction

$$(CH_3)_3COO^{\cdot} + PH \rightarrow (CH_3)_3COOH + P^{\cdot} ,$$

Chain propagation in such oxidation in the solid, like the oxidation of hydrocarbons with neighbouring tertiary carbon–hydrogen bonds in the β position[3], occurs by intermolecular and intramolecular mechanisms:



For oxidation in the solid phase, therefore, $k_2 = k_2' + k_2''/[PH]$. For 2,4-dimethylpentane $k_2''/k_2' = 90$ at 373 K if k_2' relates to a single tertiary carbon–hydrogen bond[74]. Assuming the same relation for polypropylene, with the use of $k_2 = 0.7$ and $[PH] = 22$ M, we obtain $k_2' = 0.18$ M^{-1} s^{-1}, about one-fifth of the value in the liquid phase.

Thus reaction of a peroxy-radical with a carbon–hydrogen bond takes place more slowly in a solid polymer than in the liquid phase. This is due to the effect of the rigid cage of the polymer matrix on the probability of achieving the mutual orientation of radical and bond required for the reaction. This is consistent also with the polychromatic reaction kinetics of peroxy-radicals in polystyrene[72], which cannot be explained by hindrance to translational or rotational diffusion of segments, since in this case we are dealing with a slow reaction not controlled by such diffusion of species.

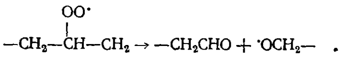
Breakdown of Macroradicals

The oxidation of polymers is accompanied by degradation of the macromolecules and a fall in the molecular mass of the polymer. The mechanism of this process still remains obscure. Since alkoxy-radicals tend to break down, but are formed by the decomposition of hydroperoxides, it was natural to attribute degradation of the macromolecules to breakdown of POOH:[48]

$$POOH \rightarrow HO^{\cdot} + PO^{\cdot} \rightarrow \text{decomposition.}$$

However, experiments on the initiated oxidation of polymers have shown that degradation begins with the appearance of peroxy-radicals long before a hydroperoxide has accumulated and begun to break down at an appreciable rate[37,75].

Tobolsky found[37] that the rate of degradation of polypropylene $W_S \propto W_i$ (with benzoyl peroxide as initiator at 363–378 K). Since in a steady state rate of initiation and of loss of radicals are equal, while tertiary peroxy-radicals also react to form alkoxy-radicals $2PO_2^{\cdot} \rightarrow 2PO^{\cdot} + O_2$, degradation was attributed to the generation of $PO^{\cdot}$ radicals and their subsequent decomposition. However, the relation $W_S \propto W_i^{1/2}$ is observed[75] in the oxidation of polyethylene (at 115°C): i.e. W_S is directly proportional to the concentration of peroxy-radicals, and rupture of a carbon–carbon bond is a first-order reaction with respect to $PO_2^{\cdot}$. By analogy with the breakdown of $PO_2^{\cdot}$ in the gas phase[2] it is suggested[75] that such rupture is effected by the reaction



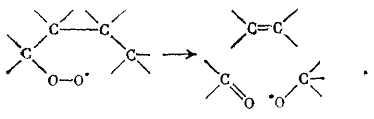
$$-CH_2-\overset{OO^{\cdot}}{\overset{|}{C}}H-CH_2 \rightarrow -CH_2CHO + {}^{\cdot}OCH_2- \ .$$

With the oxidation of methane as example, however, it has recently been convincingly demonstrated[49] that degradation in gas-phase oxidation has the mechanism

$$2RO_2^{\cdot} \rightarrow 2RO^{\cdot} \rightarrow \text{decomposition.}$$

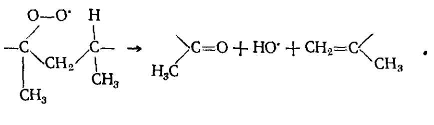
Hence there are no grounds for the first mechanism of degradation.

Marchal suggests[76] the mechanism



However, such intramolecular incorporation of oxygen of the peroxy-radical (radical substitution) is improbable, since the activation energy of this process followed by decomposition would be very high.

The most probable mechanism is breakdown of the peroxy-radical by degradative isomerisation:



VII. RELAY MECHANISM OF MIGRATION OF A FREE ELECTRON IN A POLYMER

In liquid free radicals ($R^{\cdot}$, $RO_2^{\cdot}$) migrate by diffusion, and chain termination either occurs with a diffusion rate constant ($R^{\cdot} + R^{\cdot}$, $R^{\cdot} + RO_2^{\cdot}$) or is determined by the rate of interaction of radicals ($RO_2^{\cdot} + RO_2^{\cdot}$). In a solid polymer a macroradical hardly diffuses at all[77], but segments of the macromolecule (macroradical) are displaced by thermal motion. In polymers undergoing oxidation, chains can in general be terminated by one of three mechanisms.

The first mechanism is segmental diffusion: a segment carrying the free electron, as it moves, encounters another segment, a radical, with which it interacts. Segmental diffusion provides a satisfactory explanation of the kinetics of the loss of alkyl macroradicals at low temperatures, and notably the "stepwise" character of their disappearance, which is due also to the non-uniformity of the polymer. Segmental diffusion is a slow process: e.g. in an ethylene–propylene copolymer (mol. wt. 200 000) $D = 4 \times 10^{-17}$ cm^2 s^{-1} at 220 K.[78] Displacement of a segment is restricted to an effective distance l. At the temperatures of oxidation (350–450 K) the loss of radicals is far more rapid than could be due to segmental diffusion, so that another hypothesis was required.

A second hypothetical mechanism of chain termination involved the formation of simple radicals, their rapid diffusion, and their recombination with macroradicals[79]. This hypothesis is open to several objections. Firstly, radicals of low molecular weight should appear at a rate exceeding the rate of initiation, but they can be formed only in the slow endothermic decomposition of radicals. On the assumption that termination is limited by the rate of such decomposition, it should be linear, whereas in oxidation termination is always bimolecular (Section IV). Secondly, if such active radicals as $HO^{\cdot}$ and $RO^{\cdot}$ are formed, they will react rapidly with carbon–hydrogen bonds in the polymer and, because of the low steady-state concentration, will be unable to participate in chain termination. For example, t-butoxy-radicals abstract hydrogen from tertiary carbon–hydrogen bonds in aliphatic hydrocarbons with $k = 80\,000$ M^{-1} s^{-1} at 408 K,[19] and in polypropylene with a rate of formation $rO^{\cdot} = 10^{-6}$ M s^{-1}

their steady-state concentration is ~10^{-12} M; with $[P^\cdot] = 10^{-6}$ M and $k_D = 10^8$ M^{-1} s^{-1} we obtain $W_{P^\cdot + rO^\cdot} \simeq 10^{-10}$. Substantial difficulties arise when an attempt is made to write down specific decomposition reactions. A terminal alkyl radical usually breaks down to form a monomer and a macroradical [polyethylene, polypropylene, polystyrene, poly(methyl methacrylate), etc.]; and a central alkyl macroradical mostly decomposes into a macromolecule and a macroradical. Therefore chain termination involving radicals of low molecular weight in hydrocarbon polymers undergoing oxidation is improbable in the absence of compounds of low molecular weight.

A mechanism of migration of a free electron in the form of simple radicals may develop when the polymer contains a highly active simple compound that reacts rapidly with the macroradicals. Introduction of cumenyl hydroperoxide, for example, retards the initiated oxidation of polypropylene and arrests the oxidation of polyethylene [80] by means of the reaction

$$PO_2^\cdot + rOOH \rightarrow POOH + r\dot{O}_2$$
$$r\dot{O}_2 + PO_2^\cdot \rightarrow \text{Molecular products} \ .$$

Rapid diffusion of $rO_2^\cdot$ ensures comparatively rapid termination of chains. Simple compounds such as the lower aldehydes and hydroperoxides are formed in the later stages of the oxidation of polymers as a result of the degradation of POOH, and may also be involved in transmitting free electrons along the polymer [79]. However, such a mechanism of chain termination cannot develop in the early stages of oxidation of a high polymer unless special additives are present.

Table 8. Effective $PO_2^\cdot$ loss rate constants in solid polymers at $p_{O_2} = 1$ atm.

Polymer	T, K	k_6, M^{-1} s^{-1}	Ref.
Isotactic polypropylene	383	$4 \cdot 10^5$*	71
Amorphous polypropylene	363—378	$1.1 \cdot 10^{13}$ exp (—48.5/RT)	35
Isotactic polypropylene	328—363	$1.5 \cdot 10^{21}$ exp (—119/RT)**	82
Amorphous polypropylene	331—336	$5.0 \cdot 10^{10}$ exp (—52/RT)	42
Polystyrene	247—413	$6 \cdot 10^{18}$ exp (—75/RT)	84, 85
Polystyrene	265—283	10^{14} exp (—73,5/RT)	83
Poly(methyl methacrylate)	278—310	$6 \cdot 10$ exp (—75/RT)	84, 85
Poly(methyl methacrylate)	273—292	$3 \cdot 10^{12}$ exp (—71/RT)	86
Poly(methyl methacrylate)	293	0,36	87
Poly(vinyl acetate)	347—310	$6 \cdot 10^{12}$ exp (—75/RT)	84, 85

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*Calculated from published data [71] by means of the formula $k_6 = W_i/[PO_2^\cdot]$, with $W_i = W_{O_2}^2/a^2$, in which $a = W_{O_2} W_i^{-1/2}$, taken from Ref. 38 (Table 4).

**Calculated for the amorphous phase.

A third possibility is that the free electron may migrate as a macroradical in the polymer by the so called relay mechanism [81]: the fragment of the macromolecule bearing the free electron moves by segmental diffusion, which is followed by chemical transfer of the electron to another segment, and so on, until two radicals meet and react. A relay mechanism of free-electron migration along a polymer during its oxidation is convincingly supported by the following facts. (i) The irradiation of polymers in the presence of oxygen yields free radicals, whose loss in the absence of an initiating effect is accompanied by the absorption of oxygen [43]. Several oxygen molecules are absorbed per $PO_2^\cdot$ radical lost: i.e. disappearance of the radicals is accompanied by the chain reaction

$$PO_2^\cdot \xrightarrow{PH} P^\cdot \xrightarrow{O_2} PO_2^\cdot \longrightarrow \ldots,$$

and the encounter and loss of radicals result from their relay migration. (ii) Introduction of a chemically inert solvent into the polymer increases segmental mobility and also the average distance l through which the segment carrying the free electron moves during its lifetime. Thus the "relay distance" is increased and hence also the effective rate constant of recombination of the radicals. Addition of benzene to polypropylene and polystyrene produces a very considerable increase (by factors of 10–100) in the corresponding constant for bimolecular loss of $PO_2^\cdot$. [83] (iii) Since relay migration of the free electron involves a step of chain propagation, the inequalities $E_6^{PH} > E_6^{RH}$ and $E_6^{PH} > E_2^{PH}$ (the superscripts PH and RH denote media in which E_6 has been measured for peroxy-radicals of similar structure). This is consistent with experiment: values of 48 and 52 kJ $mole^{-1}$ have been obtained for E_6 in amorphous polypropylene, and 119 in the isotactic polymer (Table 8), while for cumenylperoxy-radicals in cumene $E_6 = 25$ kJ $mole^{-1}$, [19] so that $E_6^{PH} > E_6^{RH}$; since in isotactic polypropylene $E_2 = 88$ kJ $mole^{-1}$, we have $E_6^{PH} > E_2^{PH}$. (iv) The inhibiting effect of cumenyl hydroperoxide on the initiated oxidation of polyethylene and polypropylene [80] is also consistent with a relay mechanism, since inhibition can be explained by substitution of more rapid diffusion for the comparatively slow relay mechanism.

Table 9. Segmental movement (relay distance l) in the loss of free radicals in polymers.

Polymer	Valency-transfer reaction	T, K	$10^6 l$, cm	Δt, s	Ref.
Polyethylene	$P^\cdot + PH$	363	0.5	—	90
Polypropylene	$P^\cdot + PH$	373	1.7	0.015	34
Poly(methyl methacrylate)	$P^\cdot + PH$	311	0.55	—	90
Poly(methyl methacrylate)	$P^\cdot + PH$	328	0.15	—	90
Polyethylene	$PO_2^\cdot + PH$	363	0.35	—	90
Polypropylene	$PO_2^\cdot + PH$	292	0.75	—	90
Polypropylene	$PO_2^\cdot + PH$	323	0.37	—	89
Polypropylene	$PO_2^\cdot + PH$	383	2.4	0.12	71
Polypropylene	$PO_2^\cdot + PH$	383	1.7	0.21	82
Polypropylene	$PO_2^\cdot + PH$	383	4.7	0.14	35

Two parameters—the relay distance l and the specific rate of transfer of the free electron to another segment by chemical reaction—determine the effective rate constant with which two radicals meet. In the absence of oxygen transfer of the free electron takes place by the reaction

$$P^\cdot + PH \xrightarrow{k_1'} PH + P^\cdot \ .$$

The distance l can be estimated from experimental data in three ways.

Firstly, the bimolecular rate constant for the loss of radicals in the polymer can be used. In the amorphous phase of isotactic polypropylene, for example, $k_4 = 2.7 \times 10^6$ M^{-1} s^{-1} at 373 K.[34] With a relay mechanism $k_4 = 4 \times 10^{-3} \pi N l^3 k'_1 [\mathrm{PH}] \alpha_4$ M^{-1} s^{-1}, where N is Avogadro's number, l is expressed in centimetres, and α_4 is the probability of reaction between two P$^\bullet$ radicals $< 2l$ apart. On the assumption that the reaction P$^\bullet$ + PH takes place in PH with the same rate constant as the reaction $CH_3^\bullet + CH_4$ in the gas phase, where the rate constant is 3 M^{-1} s^{-1} at 373 K,[88] we find with [PH] = 22 M, $\alpha_4 = 1$, and $k_4 = 2.7 \times 10^6$ that l = 17 nm.

Secondly, the distance l can be identified with the radius of the "cage" in which two macroradicals meet as a consequence of segmental diffusion[78]. This radius can be estimated from experimental data on the kinetics of the loss of P$^\bullet$ in the polymer by means of the equation

$$t^{-1}([\mathrm{P}^\bullet]^{-1} - [\mathrm{P}^\bullet]_0^{-1}) = k_4(1+2\sqrt{\tau/t})$$

(where $\tau = l^2/\pi D$ and $k_4 = 4 \times 10^{-3} \pi N l D$, in which D (cm^2 s^{-1}) is the diffusion coefficient and values of l are given in Table 9), describing the kinetics of the diffusion loss of P$^\bullet$ and allowing for the initially non-stationary character of the process[78]. In the presence of oxygen the relay migration of a free electron is also a chain reaction accompanied by the absorption of oxygen. This is used to estimate l (cm) from the relation between the quantity of P$^\bullet$ that has disappeared and the oxygen absorbed[89] (Table 9):

$$\Delta[\mathrm{O_2}] = l^{-3} \ln([\mathrm{P}^\bullet]/[\mathrm{P}^\bullet]_0]$$

where $\Delta[O_2]$ is expressed in mol.cm^{-3}.

When $[O_2]$ is sufficiently high and P$^\bullet$ radicals are converted rapidly into $PO_2^\bullet$, so that relay transfer is limited by the reaction $PO_2^\bullet$ + PH, we can estimate l also from the rate constants k_2 and k_6. In polypropylene chain propagation takes place both intra- and inter-molecularly at the respective rates $k''_2[PO_2^\bullet]$ and $k'_2[PH][PO_2^\bullet]$, but only the latter process is involved in the relay mechanism. By analogy with 2,4-dimethylpentane[74] we can put $k''_2/k'_2 = 90$ at 373 K and $k'_2 = 0.2k_2$, where k_2 is the overall propagation rate constant. Hence for polypropylene we obtain $k_6/k_2 = 8 \times 10^{-4} \pi N l^3 \alpha_6$, which enables l_{min} to be estimated with $\alpha_6 = 1$. Table 9 shows that segmental movements are quite large—of the order 10^{-7}–10^{-6} cm in 0.1–0.01 s—i.e. at a mean speed of 10^{-6}–10^{-4} cm s^{-1}, while $L_{\mathrm{segm}} = 10^{-12}$–$10^{-10}$ cm^2 s^{-1} at around 373 K. The comparatively high segmental mobility also ensures relatively rapid migration and meeting of free electrons during the oxidation of such polymers as polyethylene and polypropylene. Since a polymer is non-uniform, with zones differing in segmental mobility, polychromatic kinetics is observed in the recombination of radicals at low temperatures[56-59].

The relay mechanism of migration of the free electron explains also why oxidation of a solid polymer is local in character, i.e. why each chain develops and terminates within a small volume. Because of the comparatively short relay distance the displacement of the free electron during such development is around $l\nu^{1/2}$, where ν is the length of the chain; with $\nu = 30$ and $l = 10^{-6}$ cm this displacement is $\sim 5 \times 10^{-6}$ cm. Therefore a mixture of polymers, e.g. polyethylene and polypropylene, is oxidised additively[38]: $W_\Sigma = W_{\mathrm{pe}} V_{\mathrm{pe}} + W_{\mathrm{pp}} V_{\mathrm{pp}}$, where W_{pe} is the rate of the initiated oxidation of polyethylene, while V_{pe} is the fraction of polyethylene by volume. Under the same conditions the rate of oxidation of copolymers of ethylene and propylene varies non-additively with composition[38]:

$$W_\Sigma \neq W_{\mathrm{pe}} \cdot [\mathrm{-CH_2-CH_2-}] + W_{\mathrm{pp}} \cdot [\mathrm{-CH_2CH(CH_3)-}],$$

just as for a mixture of n-decane and iso-octane, because of the different activities of secondary and tertiary peroxy-radicals in acts of chain propagation and termination.

VIII. REACTIONS OF ALKYL MACRORADICALS IN POLYMERS UNDERGOING OXIDATION

1. Diffusion and Kinetic Régimes of Oxidation

The oxidation of a polymer is preceded by the dissolution of oxygen in it. In a steady state, when the rates of oxidation and dissolution are equal, the process is described by the diffusion equation

$$d^2[\mathrm{O_2}]/dx^2 = W_{\mathrm{O_2}}/D,$$

where D is the diffusion coefficient for oxygen in the polymer and x the distance from the surface. Several studies have been made at low oxygen concentrations[91,92], when the rate of oxidation $W_{\mathrm{O_2}} = \beta[O_2]$, where $\beta = k_1 k_4^{-1/2} W_{\mathrm{i}}^{1/2}$. For a film $2l$ thick the depth x distribution of oxygen is given by

$$[\mathrm{O_2}] = \gamma p_{\mathrm{O_2}} \frac{\cosh[(l-x)\sqrt{\beta/D}]}{\cosh[l\sqrt{\beta/D}]},$$

in which γ is the Henry coefficient. The formula

$$\overline{[\mathrm{O_2}]} = \gamma p_{\mathrm{O_2}} l^{-1} (D/\beta)^{1/2} \tanh[l \cdot \sqrt{\beta/D}]$$

gives the average concentration of dissolved oxygen across the film.

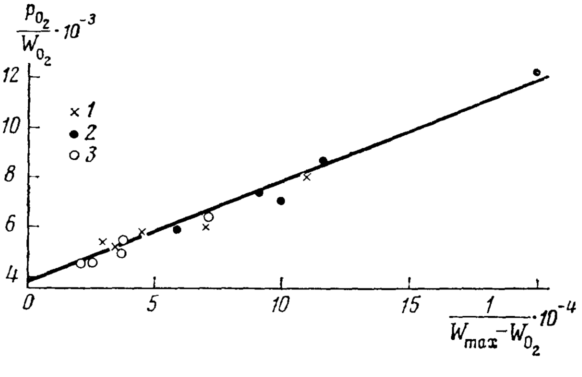


Figure 2. Dependence of $p_{\mathrm{O_2}}/W_{\mathrm{O_2}}$ on $(W_{\mathrm{max}} - W_{\mathrm{O_2}})^{-1}$ for the oxidation of polypropylene under different oxygen pressures at 371 K and initiated by different quantities (mole kg^{-1}) of benzoyl peroxide: 1) 0.031; 2) 0.062; 3) 0.1.

At small values of $l < (D/\beta)^{1/2}$ oxidation takes place in the kinetic range. Under these conditions $[O_2] = \gamma p_{\mathrm{O_2}}$ and $W_{\mathrm{O_2}} = k_1 k_4^{-1/2} W_{\mathrm{i}}^{1/2} \gamma p_{\mathrm{O_2}}$: i.e. the rate of oxidation is independent of film thickness and is proportional to $W_{\mathrm{i}}^{1/2}$. When l is large, oxidation occurs in the diffusion range, is concentrated in a thin layer $l^* = (D/\beta)^{1/2}$, and occurs at the rate $W_{O_2} = \gamma l^{-1} p_{O_2} (\beta D)^{1/2}$: i.e. it depends on D and l, and is proportional to $W_i^{1/4}$. In general the rate of oxidation is given by the formula

$$W_{O_2} = \gamma l^{-1} p_{O_2} \sqrt{\beta D} \tanh [l \sqrt{\beta / D}] \ .$$

With variation in the partial pressure of oxygen over a wider range account must be taken of the non-linear dependence of rate of oxidation on oxygen concentration, described with good approximation by the formula [34]

$$W_{O_2} = W_{max}(1 + b/[O_2])^{-1}, \ W_{max} = k_2 k_6^{-1/2} [RH] W_i^{1/2},$$
$$b = 2k_2 k_4 k_1^{-1} k_5^{-2} [PH] (\sqrt{1 + 12 k_4 k_5^{-2} k_6} - 1)^{-1}.$$

In a steady state the equation

$$\frac{p_{O_2}}{W_{O_2}} = \frac{b}{\gamma} (V_{max} - W_{O_2})^{-1} + \frac{1}{\varkappa \gamma}; \ \varkappa = 2D/l^2$$

represents the rate of oxidation in both kinetic and diffusion ranges [34]. It agrees well with experimental results (Fig. 2), and enables both diffusion and kinetic parameters κ and b to be determined. For powdered polypropylene of particle radius 10–15 μm we have κ = 0.2–0.3 s^{-1} and $b = 3 \times 10^{-5}$ M. [34]

2. Lifetime of Alkyl Radicals in an Oxidising Polymer

In a hydrocarbon or a polymer undergoing oxidation alkyl radicals ($R^{\cdot}$, $P^{\cdot}$) are interconverted into peroxy-radicals ($RO_2^{\cdot}$, $PO_2^{\cdot}$). With sufficiently long chains the rates of the two processes are almost equal. Since in the liquid phase alkyl radicals react very rapidly with oxygen ($k_1 \approx 10^8$ M^{-1} s^{-1}), it follows that $[R^{\cdot}]/[RO_2^{\cdot}] \ll 1$. In isopentane with p_{O_2} = 1 atm at 373 K ($k_2[RH] = 5$ s^{-1} [24]), for example, $[R^{\cdot}]/[RO_2^{\cdot}] = 5 \times 10^{-6}$, while the lifetime of $R^{\cdot}$ radicals is only 10^{-6} s. Under these conditions alkyl radicals have time to react only with oxygen.

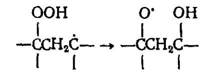
Oxygen diffuses more slowly in a polymer than in a liquid (stirring is absent, and the diffusion coefficient is smaller), so that the reaction of $P^{\cdot}$ with oxygen is far slower. In polypropylene with p_{O_2} = 1 atm at 373 K, for example, $k_1 \approx 10^6$ M^{-1} s^{-1}, [34] $\gamma = 10^{-3}$ mole kg^{-1}, [93] and the lifetime of an alkyl macroradical under these conditions is 10^{-3} s, a thousandfold the lifetime in a hydrocarbon, while the ratio $[P^{\cdot}]/[PO_2^{\cdot}] = 0.02$ on the assumption that $k_2[PH]$ = 5 s^{-1} as in isopentane. As a consequence, alkyl radicals in a polymer undergoing oxidation have time not only to react with oxygen but also to undergo other reactions.

3. Role of Alkyl Macroradicals in Chain Termination

It has been shown that in polypropylene undergoing oxidation $[P^{\cdot}]/[PO_2^{\cdot}]$ = 0.01–0.1 when p_{O_2} = 0.1–1 atm. A comparatively high relative concentration of alkyl macroradicals is present in polymers during inhibited oxidation. Inhibitors—acceptors of alkyl radicals—have a very slight effect on the oxidation of hydrocarbons [3], but inhibit that of polymers considerably more effectively [94]. For example, even at a concentration of 1mM p-benzoquinone inhibits the oxidation of polypropylene (p_{O_2} = 1 atm at 388 K), but begins to affect the oxidation of isooctane (1 atm at 353 K) only at concentrations exceeding 30mM. Moreover, such inhibitors as anthracene and 2,6-dinitrophenol, which react only with peroxy-radicals in inhibiting liquid-phase oxidation [3], terminate chains by reaction both with $PO_2^{\cdot}$ and with $P^{\cdot}$ in the oxidation of polypropylene [94]. A stable nitroxyl radical reacts with a $P^{\cdot}$ radical in polypropylene at 387 K and a rate constant of 35 000 M^{-1} s^{-1} (calculated from the ratio $k/k_1 \gamma$ [94] with $k_1 = 1.1 \times 10^6$ M^{-1} s^{-1} and $\gamma = 10^{-3}$ M atm^{-1}). Reactions of alkyl radicals play a very important part in the formation and transformation of hydroperoxy-groups (Section IX).

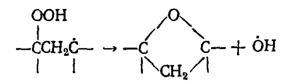
IX. FORMATION AND BREAKDOWN OF HYDROPEROXY-GROUPS

In the chain oxidation of hydrocarbons all the oxygen absorbed initially forms a hydroperoxide [3]: i.e. all the $RO_2^{\cdot}$ radicals are converted into ROOH. In polymers a discrepancy is often observed between the quantity of oxygen absorbed and the hydroperoxide formed [46,95–97]. It has been suggested [97] that in polypropylene this is due to isomerisation of the type



$$-\overset{OOH}{\overset{|}{\underset{|}{C}}}CH_2\dot{\underset{|}{C}}- \rightarrow -\overset{O^{\cdot}}{\overset{|}{\underset{|}{C}}}CH_2\overset{OH}{\overset{|}{\underset{|}{C}}}-$$

or [74]



Since the reaction $P^{\cdot} + O_2$ competes with isomerisation, fall in the oxygen pressure should be accompanied by decrease in the proportion of absorbed oxygen that is converted into hydroperoxide. This is supported by experiments [34] on the oxidation of polypropylene at different oxygen pressures, in which such a decrease is observed (Fig. 3). A decrease is observed also when a specimen of polypropylene is stretched and thus undergoes orientational cross-linking [98–100]. Kinetic data give for isomerisation of the peroxy-radical a rate constant of 1500 s^{-1} in polypropylene at 373 K. [34]

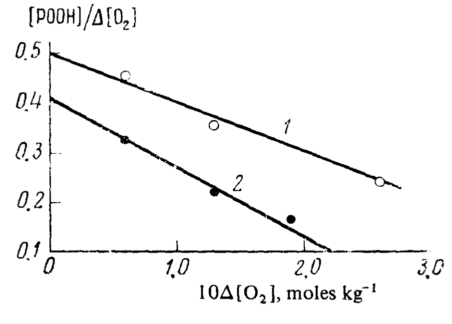
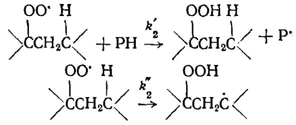
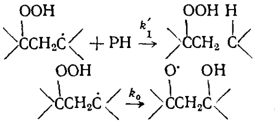


Figure 3. Dependence of $[POOH]/\Delta[O_2]$ on extent of oxidation $\Delta[O_2]$ of polypropylene initiated by benzoyl peroxide (0.064 mole kg^{-1}) at 365 K under different oxygen pressures: 1) 1 atm; 2) 0.26 atm.

Propagation of an oxidation chain in polypropylene, as in model hydrocarbons, is effected by two mechanisms—intermolecular and intramolecular—which lead to the respective formation of single and block (adjoining) hydroperoxy-groups:



Predominantly block groups are formed in the polymer, as has been demonstrated[101] by several methods. Preferential isomerisation of peroxy-radicals characterises not only polypropylene but also hydrocarbons containing several tertiary carbon–hydrogen bonds in β positions. Thus in 2,4-dimethylpentane at 373 K the ratio $k_2'[\mathrm{RH}]/k_2'' = 0.25$.[74] In polyethylene, in contrast, single hydroperoxy-groups are formed, as a consequence of the low probability of intramolecular isomerisation in n-alkanes. For example, in n-pentane at 373 K the corresponding ratio is 25,[102] a hundred times the value in 2,4-dimethylpentane. In a polymer the lifetime of an alkyl radical is much longer than in a liquid, and provides time for the reaction



Therefore the ratio between single and block groups (POOH and POOH′) depends on the oxygen pressure:

$$\frac{[\mathrm{POOH}]}{[\mathrm{POOH}]'}=\frac{k_2'}{k_2''}[\mathrm{PH}]+\frac{(k_2'[\mathrm{PH}]+k_2'')(k_0+k_1'[\mathrm{PH}])}{k_1[\mathrm{O_2}]}\ .$$

The proportion of block groups increases with rise in this pressure, but since they break down more rapidly into radicals, this leads to an increase in the effective rate constant of radical generation[103].

Thus through the concentration of oxygen in the polymer (polypropylene) the oxygen pressure has different effects on oxidation. Firstly, it affects the relation between the quantities of absorbed oxygen converted into POOH and into other groups:

$$\Delta[\mathrm{O_2}]/[\mathrm{POOH}]=1+k_0k_1^{-1}[\mathrm{O_2}]^{-1}.$$

Secondly, the ratio between the quantities of single and block POOH groups depends on the oxygen concentration and hence pressure, and this in turn affects the rate of self-initiation, since $k_{3\Sigma} = k_3[\mathrm{POOH}]/[\mathrm{POOH}]_\Sigma + k_3'[\mathrm{POOH}']/[\mathrm{POOH}]_\Sigma$. Fig. 1 shows that the higher the oxygen pressure the more rapidly does oxidation develop.

Hydroperoxy-groups are unstable, undergoing decomposition into radicals that either escape into space or undergo recombination inside the cage (with relative probabilities e and $1 - e$), as well as[34] induced chain decomposition. This last process has been demonstrated in polypropylene by an experiment involving introduction of an inhibitor and an initiator, respectively retarding and accelerating such decomposition[34]. The rate of induced chain decomposition conforms to the formula

$$W_\nu=\mathrm{const}\cdot[\mathrm{POOH}]\cdot W_i^{1/2}$$

and is consistent with the reaction scheme

$$\begin{gathered}\mathrm{POOH}\xrightarrow{k_3}\quad\text{Free radicals}\quad\xrightarrow{\mathrm{PH}}\mathrm{P\cdot}\\ \mathrm{P\cdot}+\mathrm{POOH}\xrightarrow{k'}\mathrm{POH}+\mathrm{PO\cdot}\\ \mathrm{PO\cdot}+\mathrm{PH}\rightarrow\mathrm{P\cdot}+\mathrm{POH}\ \text{(rapid)}\\ \mathrm{P^{\cdot}}+\mathrm{P\cdot}\xrightarrow{k_4}\text{Chain termination}\ .\end{gathered}$$

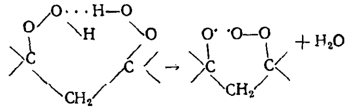
The rate of the chain decomposition of POOH will then be $k'k_4^{-1/2}W_i^{1/2}[\mathrm{POOH}]$; when the hydroperoxide itself is the source of radicals, $W_i = k_3[\mathrm{POOH}]$ and $W_\nu = k'k_4^{-1/2}k_3^{1/2}$.$[\mathrm{POOH}]^{3/2}$, which agrees with experiment[34]. In polypropylene at 365 K the coefficient $k'k_4^{-1/2} = 0.02\ \mathrm{M^{-1/2}\ s^{-1/2}}$; using the value $k_4 = 2.7\times10^6\ \mathrm{M^{-1}\ s^{-1}}$,[34] we obtain $k' = 50\ \mathrm{M^{-1}\ s^{-1}}$. Under oxidising conditions induced decomposition also takes place[34], although alkyl radicals disappear rapidly by reaction with oxygen (which is proved by comparing the rate of decomposition of POOH under oxidising conditions with its rate of decomposition into radicals).

Induced decomposition must be allowed for in calculating the probability e of the escape of radicals into space. By definition $e = k_3/2k_r$, where k_r is the rate constant of breakdown into radicals. But the total rate of decomposition of POOH is $k_r[\mathrm{POOH}] + k_\nu[\mathrm{POOH}]^{3/2}$, where $k_\nu = k'k_4^{-1/2}k_3^{1/2}$. Calculation of e from the ratio $k_3/2k_\Sigma$ will therefore give an underestimate, since $k_\Sigma > k_r$. Hence the formula $e = k_3/2(k_\Sigma - k_\nu[\mathrm{POOH}]^{1/2})$ must be used, in which k_Σ is the overall rate constant of decomposition of POOH. In polypropylene at 365 K block hydroperoxy-groups decompose with a probability $e = 0.11$ that the radicals formed will escape into space[34]; but in polyethylene at the same temperature $e = 0.5$ for the decomposition of single OOH groups[34]. Two methods—inhibitors[103] and chain oxidation[34,103]—are used to measure the formation of radicals from POOH: in the former the rate of consumption of an inhibitor W_{InH} is determined, and $W_i = fW_{\mathrm{InH}}$ if the inhibitor is consumed only by reaction with free radicals and "captures" all the free radicals; the latter method involves measuring the rate $W_{\mathrm{O_2}}$ of the POOH-initiated oxidation, when $k_i = W_{\mathrm{O_2}}^2/a^2[\mathrm{POOH}]$, in which $a = W_{\mathrm{O_2}}W_i^{-1/2}$ measured in an experiment with an initiator under the same conditions. Closely similar results are obtained by the two methods. If the inhibitor reacts directly with POOH, this can be taken into account in calculating k_i, but in such cases it is preferable to determine k_i from $W_{\mathrm{O_2}}$, since this will give more reliable results.

Table 10. Decomposition rate constants for hydroperoxy-groups in polyethylene and polypropylene.

Polymer	Oxidation conditions	T, K	k_i, $\mathrm{s^{-1}}$	Ref.
Polyethylene	in chlorobenzene at 388 K	351—403	$1.6\cdot10^{14}\ \exp(-146/RT)$	103
Polyethylene	benzoyl peroxide at 363 K	365	$5.0\cdot10^{-6}$	34
Polypropylene	in cumene at 388K	388	$5.0\cdot10^{-6}$	103
Polypropylene	in chlorobenzene at 383 K	383—413	$2.4\cdot10^{6}\ \exp(-79/RT)$	103
Polypropylene	benzoyl peroxide, 363 K, 1 atm $\mathrm{O_2}$	365	$5.0\cdot10^{-6}$	34
Polypropylene	benzoyl peroxide, 363 K, 1 atm $\mathrm{O_2}$	387	$2.8\cdot10^{-5}$	34
Polypropylene	AIBN, 358 K, 1 atm $\mathrm{O_2}$	322—370	$3.1\cdot10^{11}\ \exp(-119/RT)$	31

Table 10 gives values of k_i for POOH groups obtained by oxidising polypropylene and polyethylene. Comparison of k_i for the oxidation of polypropylene in cumene and in chlorobenzene, in which single and block hydroperoxy-groups respectively predominate, indicates that the latter type decompose far more rapidly[103], which is explained by the involvement of both OOH groups. By analogy with the bimolecular breakdown of POOH in the liquid phase the most probable mechanism is



which energetically is far more advantageous that unimolecular decomposition with rupture of a single O–C bond. Furthermore, such bimolecular decomposition occurs in the liquid phase in preference to the reaction

$$ROOH + RH \rightarrow RO^{\cdot} + H_2O + R^{\cdot}$$

owing to formation of a hydrogen bond between two ROOH groups.

The mechanism of the breakdown of single hydroperoxy-groups is still obscure. Two possibilities are unimolecular decomposition at the peroxy-bond and reaction of POOH with a carbon–hydrogen bond. If radicals are generated by the latter reaction, it must be expected that $k_3^{pe} < k_3^{pp}$, since carbon–hydrogen bonds are more stable in polyethylene than in polypropylene. However, closely similar values are obtained: $k_3 = 10^{-5}$ s^{-1} in polyethylene and 0.6×10^{-5} s^{-1} for single hydroperoxy-groups in polypropylene at 398 K.[103] For a unimolecular reaction, on the other hand, k_3 should not depend on the length of the alkyl substituent and should have similar values in gaseous and condensed phases. However, it is substantially larger (hundredfold at 393 K) in liquid and solid than in the gas phase[104]. Therefore further investigation is required on the mechanism of the breakdown of POOH and ROOH in solid and liquid phases respectively.

X. CONCLUSION

As we have become convinced, the oxidation of carbon-chain polymers in the solid phase and of hydrocarbons in the liquid phase has a single mechanism—a self-initiated chain reaction involving propagation of alkyl and peroxy-radicals with bimolecular chain termination—characterised by certain kinetic features: under conditions of initiated oxidation $W_{O_2} \propto W_i^{1/2}$; at low oxygen pressures $W_{O_2} \propto p_{O_2}$ under both kinetic and diffusion régimes of oxidation; W_{O_2} is independent of sufficiently high oxygen pressures; and in the initial stage of autoxidation $\Delta[O_2] \propto t^2$. Furthermore, a solid polymer as medium in which oxidation is developing has several important characteristics, leading to the following features of chain oxidation typical only of solid-phase oxidation.

1. The free electron (as a $P^{\cdot}$ or $PO_2^{\cdot}$ macroradical) moves along the polymer in a chain oxidation mostly by a *relay mechanism* involving segmental diffusion and transfer of the electron from one segment to another by the reactions

$$P^{\cdot} + PH \rightarrow PH + P^{\cdot} \text{ и } PO_2^{\cdot} + PH \rightarrow POOH + P^{\cdot} .$$

2. As the cage walls in a polymer are formed by *slowly moving segments of macromolecules* and the form of the cage relaxes slowly, a *polymer matrix* differs from a non-polar liquid in influencing the rate of primary steps involving radicals: the more rigid the matrix, i.e. the slower are molecular displacements in it, the lower the rate of the primary step.

3. Because of the comparatively slow diffusion of oxygen in the polymer and its lower solubility *alkyl macroradicals* live for a relatively long time in the polymer, and undergo together with $P^{\cdot} + O_2$ various other reactions, such as isomerisation, interaction with an adjacent carbon–hydrogen bond, reaction with POOH, and reactions with inhibitors effecting chain termination.

4. As a consequence of the *inhomogeneity of a polymer* different regions are oxidised at different rates. In polyethylene and polypropylene, for example, oxidation affects the amorphous phase almost alone, while the crystalline phase is oxidised only slightly.

5. Because of the *high molecular mass of a polymer* the comparatively rare (slow) *acts of rupture* of a carbon–carbon bond, which are almost imperceptible in the oxidation of the lower hydrocarbons, appear at an early stage in the oxidation of polymers.

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Effect of Mobility of Medium on Formal Kinetics of Chemical Reactions in a Condensed Phase

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Chemical kinetics is examined under conditions such that the medium is quite mobile (classical kinetics), when it can be regarded as immobile throughout the process (i.e. with kinetic non-equivalence of reactant species), and also under intermediate conditions of kinetic non-equivalence maintained only during the lifetime of the leading active species. Methods for studying the kinetics of variation in reactivity due to change in the local properties of the medium are discussed, and reasons for the levelling of reactivity in a series of structurally different molecules on passing from liquid to solid media are analysed. The bibliography contains 37 references.

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I. INTRODUCTION

In a condensed phase every species is subject to the time-variable influence of the surrounding molecules of the medium. This affects the probability of occurrence of primary steps of chemical conversion. Herein lies the chief cause of the qualitative difference between a primary chemical step in a condensed phase and the corresponding step in the gas phase. In the study of, for instance, a bimolecular reaction in the latter it is sufficient to examine the interaction of the two reactants in a vacuum, for the remaining species have no appreciable effect on this process.

A substantially different situation obtains in a condensed phase, in which molecules of the medium influence all stages of chemical interaction. The properties of the molecules govern transport of reactant species towards each other and the probability of their meeting. The medium has a considerable effect also on the actual chemical reaction: surrounding molecules may prevent rearrangement of reactant species, the electromagnetic field due to the medium changes the relation between different possible primary reaction paths, and considerable exchange of energy takes place between medium and reactants. Thus the medium plays a part in organising the primary step of chemical conversion[1]. The molecular motion of the medium produces continuous change in its local properties in the immediate environment of the reactants. The formal kinetics of a chemical process depends on the rapidity of variation in these local properties influencing the reactivity of the reactants.

The present Review examines the influence of the dynamics of the variation in these local properties of the medium on the kinetics of a chemical process, and discusses qualitative differences between the description of reaction kinetics in a condensed medium and the classical kinetics of gas-phase reactions. The problem of which local properties cause the variation in reactivity is almost completely ignored. Nor are more complicated aspects of the influence of the medium on chemical kinetics considered (the structure and the reasons for the formation of more or less stable complexes of the reactants with the medium, or solvate sheaths, the influence of the supermolecular structure of the medium on the process, etc.). Consequently the Review regards a condensed phase as a macroscopically homogeneous medium, non-uniformity in which can arise only at a cellular level, i.e. at distances of the order of the dimensions of the reactant molecules.

II. FORMAL KINETICS OF REACTIONS IN A CONDENSED PHASE

Two main approaches are usually made to the kinetics of chemical reactions in the gas phase. If the process is sufficiently slow, the reactants have enough time to exchange energy with the medium, so that they are in a nearly equilibrium distribution with respect to energies, rates, and distances apart. Under these conditions the law of mass action is used to describe the formal kinetics: the rate of a given primary process is proportional to the product of the reactant concentrations. The coefficient of proportionality is a measure of the rate constant; its temperature dependence is given by the Arrhenius equation.

In the other extreme case, in which chemical interaction produces either a chemically unstable species or a highly reactive species, i.e. one that undergoes further chemical changes only through several collisions with other molecules, the kinetic description is based neither on the law of mass action nor on the concept of the reaction rate constant but on the probability of involvement of the species in a particular reaction after its formation.

In a condensed phase the probability of chemical reaction may be influenced not only by the properties of the reactants but also by the local properties of the medium. In general, therefore, the rate constant of a chemical reaction occurring in a condensed phase is a function of some parameter u representing such local properties. We shall not now specify the physical nature of u, since various media may have different effects on various primary chemical processes. The parameter may represent the formation of specific complexes, the effect of the electromagnetic field of the medium, steric hindrance, direct involvement of molecules of the medium in the chemical reaction. In general, if the local properties governing the probability of chemical reaction depend on several parameters, u is a vector.

On the above approach the kinetics of the variation in the macroscopic concentration of a substance A involved e.g. in a simple unimolecular reaction is described by the integrodifferential equation

$$\frac{d[A]}{dt}=\int\frac{dA(u)}{dt}\,du=\int k(u)\,A(u)\,du, \qquad (1)$$

where $A(u)$ is the distribution function of the concentration of A in terms of the parameter u, and $k(u)$ is a function relating the effective rate constant of chemical conversion of A to u. Equation (1) leads to the usual exponential law of variation of [A], known as the first-order kinetic equation, in only two cases—(i) if the rate constant varies little with the local properties of the medium, i.e. if

$$k(u)=\text{const}, \qquad (2)$$

and (ii) if these local properties vary so rapidly in comparison with the rate of chemical reaction that $k(u)$ can be replaced throughout the process by a mean value and removed from the integral on the right-hand side of Eqn. (1).

Thus the rate of variation in the local properties of the medium, i.e. the relationship between three temporal parameters—the characteristic time of chemical conversion τ_x, the lifetime of the active centre effecting the process τ_e, and the correlation time between the reactants over all states in the medium τ_c—must be taken into account in order to describe the kinetics of a process in a condensed phase. Here τ_x is a macroscopic parameter of the process, representing the time for significant change in composition of the reactants; it can be characterised by the reciprocal of the relative rate of change in concentration of the reactants. For a unimolecular reaction τ_x is then the reciprocal of the rate constant k_1:

$$\tau_x=1/k_1,$$

For a bimolecular reaction it is given by the reciprocal of the product of the rate constant k_2 and the instantaneous concentration c:

$$\tau_x=1/k_2c.$$

The quantity τ_e may represent the time from the instant of formation of an active centre until its destruction or conversion into another active centre. For molecular decomposition τ_e is of the order of the time of rearrangement of the molecule during decomposition, i.e. the vibration period of the atoms in the molecule. It will be considerably longer when the molecule breaks down into active species, e.g. radicals. Thus for radicals that have escaped into the bulk of the specimen

$$\tau_e=1/k_t\,[R],$$

where k_t is the rate constant of such loss. The lifetime of an oxidation chain may also correspond to τ_e:

$$\tau_e=1/\sqrt{w_ik_t},$$

where w_i is the rate of formation of active centres in the system. Different values of τ_e may apply to different primary steps in the same composite process. For example, τ_e is considerably shorter for active centres that recombine in the cage in which they were formed than for those that have escaped from the cage and recombine in the bulk of the specimen.

The correlation time τ_c between species in a medium is the time during which a reactive species is able to exist in all possible states in which it has different reactivities. It is determined by how rapidly those properties of the reactant species that determine reactivity change as a result of the relative motion of the species and the molecules of the medium. The magnitude of τ_c can be judged to some extent from the correlation time of a paramagnetic probe or the time of depolarisation of luminescence. There is some analogy between τ_c and the time of establishment of thermal equilibrium between the species and the medium. In this sense we can speak of a correlation time even in gas-phase systems. Since energy is exchanged in the gas phase by collisions between particles, the correlation time for energy is of similar order of magnitude to the time between two collisions. In a condensed phase any particle is almost always in a state of collision with some particle of the medium, and τ_c is then very short—around a few picoseconds—for energy. Correlation times with other characteristics of reactant species therefore have greater practical value.

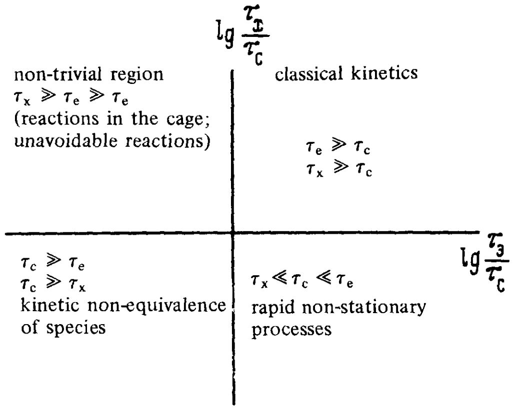

Figure 1. Qualitative variation in kinetics of chemical processes with the relationship between the characteristic times of their occurrence and the correlation time of the species in the medium.

The formal kinetics of chemical processes are qualitatively different depending on the relationship between the above three characteristic times. If in a plane $\lg(\tau_e/\tau_c)$ is plotted as abscissa, and $\lg(\tau_x/\tau_c)$ as ordinate (Fig. 1), every specific chemical process can be represented by a point in this plane†. The upper right-hand corner contains processes for which the correlation time is the shortest of the three:

$$\tau_c\ll\tau_x;\ \tau_c\ll\tau_e. \qquad (3)$$

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† The three characteristic times (primarily τ_x) may vary during change in the composition of the system due to the chemical process. In the plane, therefore, the chemical reaction is represented by a segment of a curve. For the sake of simplicity, however, we shall henceforward neglect the linear dimensions of this segment: more precisely, we shall consider only those processes during which change in the relation between the characteristic times is insignificant.

All the primary steps then occur under the same conditions, so that the kinetic description is formally analogous to that in the gas phase. The effective rate constants of the primary reactions will equal the average values of the primary constants over all possible values of *u* realisable in the given medium under the given conditions. This part of the coordinate plane is the region in which all the classic concepts of chemical kinetics are valid.

The lower left-hand corner contains processes for which the correlation time is the longest of the characteristic times:

$$\tau_c \gg \tau_x;\ \tau_c \gg \tau_e. \tag{4}$$

This means that the process occurs as if in a completely "frozen" medium, with the reactant species under unchanged conditions throughout the process, but these conditions may differ for different species, so that the species may be kinetically non-equivalent. Under these conditions the rate of a chemical process is not proportional to the macroscopic concentration of the reactant species, but depends on how the latter are initially distributed with respect to the parameters determining their reactivity in the condensed medium, and how this distribution varies with time. The kinetics of such processes are often termed *polychromatic*[2], since, in contrast to the usual monochromatic processes, the rate of each primary reaction is then defined not by a single rate constant but by a set of rate constants governed by the local conditions. Since the medium is "frozen", the condition of each species remain unchanged throughout the process: i.e. it appears to "remember" its conditions when the process began. The equations of classic kinetics then describe not the variation in the macroscopic concentration of the reactants but that of the density of distribution among various local conditions $A(u)$.

In the above example of a unimolecular reaction $k(u)$ may differ for different $A(u)$ functions. The kinetics of the variation in $A(u)$ will therefore be described for each value by the exponential relation

$$A(u) = A(u)_0 e^{-k(u)t}, \tag{5}$$

but the exponent will differ for different values of *u*. The variation in the macroscopic concentration of the substance A, given by the equation

$$[A] = \int A(u)_0 e^{-k(u)t} du \tag{6}$$

may thus not be exponential in character. A common feature of reactions under these conditions (4) is the kinetic non-equivalence of species of the same chemical structure, which remains unchanged throughout the process.

As we move upwards from the lower left-hand corner of the plane (Fig. 1), we may enter a range of processes in which τ_X is comparable with τ_C. In describing them we must bear in mind that the density of distribution of concentration may vary with *u* as a consequence not only of chemical change but also of the mobility of the medium. In the case of a unimolecular reaction the kinetics of the variation in $A(u)$ will thus be determined by a more complicated equation than if the law of mass action were formally obeyed:

$$\frac{dA(u)}{dt} = -k(u)A(u) + \frac{\partial A(u)}{\partial u}\frac{\partial u}{\partial t}. \tag{7}$$

Under these conditions it is obviously not always possible to obtain an exponential variation of $A(u)$ with time.

Still higher, in the top left-hand corner of the plane, are situated processes for which the correlation times have intermediate values:

$$\tau_x \gg \tau_c \gg \tau_e. \tag{8}$$

When condition (8) is satisfied, the process takes place under a peculiar quasi-stationary régime. Any reactant species may initiate chemical conversion independently of its state at the start of the process: i.e. the rate of variation of the macroscopic concentration of a reactant, as in classical kinetics, is proportional to its instantaneous macroscopic concentration.

Another large region comprises complicated processes for which $\tau_X < \tau_e$. They lie on the plane to the right and below the 45° line through the origin. This is a region of so called non-stationary processes, for which the lifetimes of the active centres are comparable with the times required for large degrees of conversion. Certain branched-chain reactions can evidently be included here. The present Review will not discuss processes of this kind: it may merely be noted that, when the relations between the characteristic times correspond to the lower half of the plane, their description must allow for the possible kinetic non-equivalence of the reactant species.

III. KINETICS WITH COMPLETE KINETIC NON-EQUIVALENCE OF REACTANT SPECIES

Under conditions such that reactant species of the same chemical structure are completely equivalent kinetically ($\tau_C \ll \tau_e$, $\tau_C \ll \tau_X$) the kinetics of a chemical process does not differ fundamentally from that of a gas-phase process, as already mentioned. Departures from classical views arise only in the description of very fast processes, whose rates are controlled by diffusion. Rate constants of such processes vary with time in conformity with Waite's equation[3,4]. However, deviations of this kind occur both in condensed-phase and in gas-phase reactions. Therefore the present Review will not survey the kinetics of such chemical processes, occurring under conditions of actual kinetic equivalence of species.

If the process occurs under the directly opposite conditions, i.e. if the correlation time is much shorter than the other characteristic times, the kinetic description differs qualitatively from that for a gas-phase process, since reactant species of the same chemical structure may be kinetically non-equivalent. It is not altogether a simple matter to realise such a process: on the one hand, it is necessary that the local properties of the matrix should remain unchanged throughout the process: on the other hand, a chemical process is usually caused by some changes in properties in the immediate vicinity of a molecule of the starting material or is due to the transport of reactant species towards each other. These difficulties probably explain why heterogeneous processes at a gas-solid interface were the first to be examined in terms of kinetic non-equivalence: species on a non-uniform solid surface are under kinetically non-equivalent conditions with respect to species arriving from the gas phase and therefore kinetically equivalent.

During the 1930s Ya. B. Zel'dovich, M. I. Temkin, and S. Z. Roginskii made a large number of studies on such chemical reactions, the results of which were summarised in a monograph[5]. They developed mathematical methods for describing the kinetics, and showed how the form of distribution of reactants among non-equivalence parameters could influence the process, as well as how the form of distribution could be estimated from kinetic data.

Ideas on the kinetic non-equivalence of reactant species involved in macroscopically homogeneous processes were first used in the 1950s to early 1960s to describe the kinetics of the annealing of radiation defects[6,7] and of the loss of free radicals at low temperatures[2,8,9]. The kinetics of such processes could be described in terms of the so called polychromaticity of the rate constant (Section II).

However, the loss of active centres in a solid matrix is not an altogether convenient process for studying the kinetic non-equivalence of reactant species, since the mechanism of their mutual approach is not always entirely clear. For example, a simple mechanism of free diffusion towards one another in the solid polymer cannot be assumed for such large species as macromolecular radicals. Therefore discussion of the kinetic non-equivalence of radicals has been widely accompanied by that of the mechanism of migration of an active centre, e.g. a valence, through a polymer matrix[10], the possible role of relatively simple impurities in this process[11], possible dimensions for microheterogeneities that might explain the observed rules without recourse to ideas on the kinetic non-equivalence of species in a macroscopically homogeneous medium. For example, a model has been suggested involving fluctuations of the free volume in a solid matrix[12]; in fact it could explain the results in terms of the kinetic equivalence of reactant species. Serious consideration has been given also to a model of controlled diffusion of the process in a homogeneous medium[13,14], providing a formally rigorous explanation of the kinetics of the initial stage of loss of free radicals, but yielding overestimates of the radii of interaction between active centres.

The main evidence for kinetic non-equivalence of species in processes of this kind is provided by the peculiar form and the temperature dependence of the kinetic curves for the variation in reactant concentrations. With change in temperature the process almost ceases after not very large changes in reactant concentrations, although no products capable of inhibiting the reaction have accumulated in the system. Nor is such cessation due to the establishment of any equilibrium. Actually, the process is not completely arrested, but undergoes a so called kinetic termination. The semi-logarithmic form of the kinetic curve, with $[A]/[A]_0$ plotted against $\ln t$, is a straight line extending to high degrees of conversion.

The above form of kinetic curve can easily be explained on the assumption of a first- or second-order reaction whose rate constant k has a wide distribution ($k_{max}/k_{min} \gg 1$), and that the reactants are initially uniformly distributed with respect to the non-equivalence parameter s, which is exponentially related to the rate constant and varies from zero to some value S:

$$k = k_{max}\,e^{-s} \quad (0 \leqslant s \leqslant S). \tag{9}$$

The kinetics of the variation in the macroscopic concentration of the initial substance A under these conditions is governed by an equation analogous to (6):

$$-\frac{d[A]}{dt} = \frac{1}{S}\int_0^S k_{max}\,e^{-s}A^n(s)\,ds, \tag{10}$$

where $1/S$ is a normalising factor, and n the order of the primary reaction, while the density of distribution $A(s)$ changes with time in conformity with the equation

$$-\frac{dA(s)}{dt} = k_{max}\,e^{-s}A^n(s) \tag{11}$$

If n is not too large and the initial distribution is uniform ($A(s) = [A]_0/S$ at $t = 0$), Eqns. (10) and (11) can be solved[15] quite accurately in the form

$$[A] \simeq -\frac{[A]_0}{S}[\ln(k_{max}[A]_0^{n-1}) - S + \ln t] \tag{12}$$

with $1 < k_{max}[A]_0^{n-1}t < e^S$. For $n = 1$ the more exact solution

$$[A] = -\frac{[A]_0}{S}[\ln(1.76k_{max}) - S + \ln t] \tag{13}$$

was obtained[16].

The specific experimental procedure, i.e. kinetic study of the loss of active centres at different temperatures, made it natural to assume that kinetic non-equivalence of species was due to different heights of the energy barrier opposing chemical reaction. This corresponded formally to a distribution of rate constants according to activation energies:

$$S = \frac{E_{max} - E_{min}}{RT}. \tag{14}$$

However, no evidence was found to support this hypothesis. Similarly, for a long time only kinetic evidence was available for the view that the peculiar kinetics of such chemical processes in a solid phase might be due to kinetic non-equivalence of species in a macroscopically homogeneous medium.

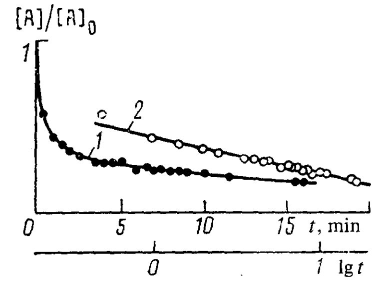

Figure 2. Destruction at 116 K of radical-pairs formed by the low-temperature (77 K) photolysis (300–400 nm) of frozen solutions of tetraphenylhydrazine in toluene: 1) kinetic curve; 2) semi-logarithmic transform (Eqn.12).

Direct evidence for such views was obtained only when effectively unimolecular processes, uncomplicated by a mechanism of approach of reactant species, began to be examined in terms of kinetic non-equivalence, and also when it became possible to halt a chemical reaction by different methods, and during the period of arrest to change the reactivity distribution of species without any change in the chemical composition of the system. The change in the effective rate of the process after such interruption served both as evidence of the validity of the model of kinetic non-equivalence of species and as a measure of the change in their reactivity distribution.

The first effectively unimolecular process examined from this point of view was the destruction of radical-pairs[15]. Electron spin resonance showed that pairs of radicals 3–6 Å apart can be generated in solutions of certain organic compounds. For example, pairs with the radicals 4 ± 0.2 Å apart have been recorded in a solution of tetraphenylhydrazine in toluene. The destruction of such radical-pairs obeys "stepwise" kinetics corresponding to Eqn. (13).

Fig. 2 shows an example of a kinetic curve for the destruction of radical-pairs and its transform plotted in the variables of Eqn. (12). These results can be explained on the assumption that the width of the distribution of the rate constants exceeds a thousandfold. Accepting in conformity with formula (9) a rectangular distribution with respect to s for the species whose decay is plotted in Fig. 2, we find that $S = 10$. It was suggested[15] that the distribution of rate constants was due solely to the distribution of activation energies and found that $\delta E = 2.3 \pm 1$ kcal mole^{-1}. Because of the narrow temperature range (100–120 K) in which the kinetics of pair destruction could conveniently be recorded, it could not be established whether the distribution of rate constants was determined by the activation energy or the pre-exponential factor. Nevertheless, since the distance between the radicals in a pair is small and almost the same for all pairs, the observed kinetics cannot be explained by peculiarities in the mutual approach of radicals. In fact a pseudounimolecular reaction takes place, whose efficiency can be influenced only by the local environment of the reacting species. It was thus shown[15] that chemical reactions could actually occur under conditions of kinetic non-equivalence of the reactant species when the time during which the local properties of the medium remain constant exceeds significantly the other characteristic times of the process.

However, kinetic non-equivalence of reactant species could be observed especially clearly in photochemical reactions, the first example being the photo-oxidation of fused-ring hydrocarbons (anthracene, naphthacene, rubrene)[16,17]. This reaction involves singlet oxygen formed on interaction between a hydrocarbon molecule in a triplet state and a molecule of ordinary triplet oxygen. The product—a transannular peroxide—can be formed by reaction of singlet oxygen either with the same hydrocarbon molecule or with another, to which it diffuses through the medium. Singlet oxygen is a relatively small molecule, probably differing little in mobility from an ordinary oxygen molecule. Therefore the character of the diffusion of this active species in any medium is known, and in quantitative descriptions use can quite confidently be made of data on diffusion coefficients of diatomic gases, which have been measured in many media.

The kinetic scheme of the photo-oxidation of a fused-ring hydrocarbon can be written

$$\begin{gathered}
\mathrm{A} + h\nu \rightarrow \mathrm{A}^* \rightarrow \mathrm{A}^{\mathrm{T}}, \\
\mathrm{A}^{\mathrm{T}} + {}^3\mathrm{O}_2 \xrightarrow{k_0} \mathrm{A} + {}^1\mathrm{O}_2, \\
\mathrm{A}^{\mathrm{T}} + {}^3\mathrm{O}_2 \xrightarrow{k_{r0}} \mathrm{AO}_2, \\
\mathrm{A} + {}^1\mathrm{O}_2 \xrightarrow{k_r} \mathrm{AO}_2, \\
\mathrm{Q} + {}^1\mathrm{O}_2 \xrightarrow{k_q} {}^3\mathrm{O}_2, \\
{}^1\mathrm{O}_2 \xrightarrow{k_d} {}^3\mathrm{O}_2,
\end{gathered} \tag{15}$$

where A, A*, and A^{T} are molecules of the oxidisable compound in ground, excited, and triplet states, ${}^3\mathrm{O}_2$ and ${}^1\mathrm{O}_2$ are oxygen molecules in the triplet ground and the singlet states, Q is the quenching agent, and AO_2 is the transannular peroxide; the symbols above the arrows denote the corresponding rate constants.

According to the law of mass action, under quasi-stationary conditions with respect to singlet oxygen, the rate of change of the concentration of the oxidisable compound should be given by the equation

$$\frac{\mathrm{d}[\mathrm{A}]}{\mathrm{d}t} = \alpha\left[1 - \gamma\left(1 - \frac{(k_r/k_d)\cdot[\mathrm{A}]}{1 + (k_r/k_d\cdot[\mathrm{A}] + (k_q/k_d)[\mathrm{Q}]}\right)\right][\mathrm{A}], \tag{16}$$

where α is the product of the probability of absorption of a light quantum by an oxidisable molecule in unit time and the quantum efficiency η of formation of singlet oxygen, while $\gamma = k_0/(k_0 + k_{r0})$ is the probability of the escape of singlet oxygen into space.

However, Eqn. (16) describes the kinetics right up to high degrees of conversion only when photo-oxidation takes place in a sufficiently fluid medium. In solid polymers at temperature considerably below the glass point it describes satisfactorily only the initial stage: at later stages the process slows down significantly more rapidly than is required by Eqn. (16). Yet no data have been obtained on the occurrence in the system of any primary steps other than those listed in scheme (15). The kinetics of the variation in the concentration of the oxidisable compound is determined solely by the quantity of light incident on the specimen, independent of its intensity. This indicates that no two-quantum processes occur, interaction between intermediate species is absent, and a sufficient quantity of oxygen diffuses into the specimen. Reactant concentrations can be recorded during the process both from the variation in the absorption spectra and from the change in intensity of fluorescence of the initial substance. Hence no quenching agents are formed during the process.

The observed kinetics was explained on the hypothesis of a non-equivalent environment of the oxidisable molecules. Because of the relative immobility of the polymer matrix the relative proportion of molecules in an environment favourable for oxidation diminishes during the process, and hence also the effective overall quantum efficiency. This hypothesis has been confirmed by direct experiment[17,18]. It was found that photo-oxidation takes place significantly more efficiently if the process is periodically interrupted and the specimen is heated in the dark to temperatures close to the glass point. This affects neither the concentration of the oxidisable substance, its absorption and fluorescence spectra, nor the quantum efficiency of fluorescence. However, after such thermal activation the process conforms to Eqn. (16) until high degrees of conversion are reached, provided that the thermal activation is conducted at a sufficiently high temperature for a sufficiently long time, sufficiently frequently, and after equal periods of illumination.

Such a result was obtained in various polymer matrices with thermal activation at ~20 deg below the glass point for 10–20 min. In polypropylene and BMK-5 (a copolymer of methacrylic acid and butyl methacrylate having $T_{\mathrm{gl}} = 40\,^\circ\mathrm{C}$) at room temperature the process satisfies Eqn. (16), and is uninfluenced by thermal activation. The explanation for these results is that the thermal activation increases the mobility of the polymer matrix, permitting restoration of the original reactivity distribution of the reactants. In polypropylene and BMK-5 the initial distribution remains unchanged throughout the process because the molecular mobility of the matrix is adequate at temperatures close to or above the glass point.

For a quantitative description of the results a model was proposed in which the kinetic non-equivalence of the oxidisable molecules was attributed to differences in permeability to singlet oxygen of the surrounding cage walls. Permeability can be characterised by the parameter u_0 occurring as a factor in the primary formation and decomposition rate constants k_1 and k_2 of the "singlet oxygen–oxidisable substance" pair. Provided that spontaneous breakdown of $^1O_2$ molecules in the cage can be neglected, k_r and γ will then be given by the formulae

$$k_r = \frac{k_1 k_3 u_0}{k_2 u_0 + k_3}, \qquad (17)$$

$$\gamma = \frac{k_2 u_0}{k_2 u_0 + k_3}, \qquad (18)$$

where k_3 is the oxidation rate constant in the pair.

The parameter u_0 has different values for different molecules of the oxidisable substance, but remains unchanged throughout the process in the absence of thermal activation. On such a model the form of the kinetic curve for consumption of the oxidisable compound is determined not only by the magnitude of the kinetic parameters but also by the kinetics of the change in the distribution function $\rho(u_0)$ of oxidisable molecules among cages differing in permeability. Assuming that the initial form of distribution is independent of the macroscopic concentration of the oxidisable compound, while the local concentration of singlet oxygen corresponds to its average concentration in the specimen, we obtain for the kinetics of variation in the concentration of the oxidisable substance, instead of (16), the equation

$$\frac{d[A]}{dt} = -(\alpha I_1 + k_1 I_2 [^1O_2]) k_3 [A], \qquad (19)$$

in which

$$I_1 = \int \frac{\rho(u_0)\, du_0}{k_2 u_0 + k_3}; \quad I_2 = \int \frac{u\rho(u_0)\, du_0}{k_2 u_0 + k_3}.$$

The distribution $\rho(u_0)$ is normalised only at zero time: $\rho(u_0)du_0 = 1$ at $t = 0$.

If the concentration of singlet oxygen $^1O_2$ is quasi-stationary, we find that

$$[^1O_2] = \frac{\alpha k_2 I_2 [A]_0}{k_1 k_3 I_2 [A]_0 + k_d}. \qquad (20)$$

Substitution of (20) in (19) yields the equation

$$\frac{d([A])/[A]_0)}{dt} = -\alpha k_3 I_1 - \frac{\alpha k_1 k_2 k_3 I_2^2 [A]_0}{k_1 k_3 I_2 [A]_0 + k_d} \qquad (21)$$

which describes the variation in concentration of the oxidisable substance right until high degrees of conversion are reached.

We can make a similar approach to the more general case, taking into account the quenching of $^1O_2$ molecules in the pair with rate constants k'_d and a possible difference in probability of chemical interaction in pairs formed after absorption of a light quantum and in those formed after an encounter between $^1O_2$ and an oxidisable molecule. With rate constants and parameters corresponding to pairs of the former type primed, the appropriate equation is

$$\frac{d([A]/[A]_0)}{dt} = -\alpha\left(k'_3 I'_1 + \frac{k_1 k'_2 k_3 I_2 I'_2 [A]_0}{k_1 (k_3 + k'_d) I_2 [A]_0 + k_d}\right), \qquad (22)$$

in which

$$I'_i = \int \frac{u_0^{i-1}\rho(u_0)\, du_0}{k_3 + k'_d + k_2 u_0}.$$

The time dependence of the distribution $\rho(u_0)$ normalised at zero time conforms to an equation analogous to (19):

$$\frac{d\rho(u_0)}{dt} = -\alpha \frac{k_3}{k_2 u_0 + k_3}\left(1 + \frac{k_1 k_2 u_0 I_2 [A]_0}{k_1 k_3 I_2 [A]_0 + k_d}\right). \qquad (23)$$

The complexity of the solution of (23) is due to the variation of the integral I_2 with time. At low concentrations of the oxidisable substance terms containing I_2 can be neglected, and (23) can be solved similarly to (11). Assuming that the probability of chemical interaction in a pair is related exponentially to some parameter s_0 distributed uniformly between 0 and S_0[‡]

$$\frac{k_3}{k_2 u_0 + k_3} = e^{-s_0}, \qquad (24)$$

we obtain instead of (23) the equation

$$\frac{d\rho(s_0)}{dt} = \frac{1}{S_0} \alpha e^{s_0} \rho(s_0) \qquad (25)$$

which is analogous to (11).

If we neglect also diffusion of oxidisable molecules through cages having different values of s_0, the kinetics of the variation in the concentration of the oxidisable compound will be described by an equation analogous to (13):

$$[A] = [A]_0 \left(1 - \frac{1}{S_0} \ln(1.76\alpha t)\right). \qquad (26)$$

At high concentrations of A we find an approximate solution analogous to (12):

$$[A] = [A]_0 \left[1 - \frac{1}{S_0} \ln\left(Z_1 \alpha t \frac{Z_2}{1 + Z_2 - \alpha t}\right)\right], \qquad (27)$$

where $Z_2 = k_d/k_1 k_3 I_2[A]_0$ and Z_1 is a factor exceeding unity (but in the present case probably not exceeding 2) characterising the form of the $\rho(u_0)$ kinetic curve. The initial rate under these conditions is given by

$$\left(\frac{d([A]/[A]_0)}{dt}\right)_{t=0} = -\alpha Z_1 \left[\frac{1 - e^{-S_0}}{S_0} - Z_2 \left(1 + \frac{1 - e^{-S_0}}{S_0}\right)\right]. \qquad (28)$$

With a sufficiently wide distribution Eqn. (28) can be simplified to

$$\left(\frac{d([A]/[A]_0)}{dt}\right)_{t=0} = -\alpha Z_1 \left(\frac{1}{S_0} - Z_2\right). \qquad (29)$$

In the study of the destruction of free radicals it is usually difficult to determine the initial rate, since the specimen heats up during the reaction, so that the initial stage takes place at a lower temperature than the process as a whole. Such difficulties do not arise with a photochemical process, which begins almost without inertia. Comparison of data on its initial rate with the kinetics of variation in concentration at later stages can therefore be used for quantitative verification of the above ideas[17,18].

Thus ideas on the kinetic non-equivalence of reactant species have provided a kinetic description of photo-oxidation, which is formally more complicated than the destruction of free radicals. However, photo-oxidation of hydrocarbons can be conducted under conditions such that the kinetics are simpler. At low concentrations of the oxidisable substance, when reactions of singlet oxygen that has escaped from the cage in which it had been formed

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[‡] If the ratio $k_2 u_0/k_3 \gg 1$ for all u, the significance of S_0 is a quantity proportional to the free energy of activation of the chemical reaction: $S_0 = \Delta G/RT = \Delta S/R + E/RT$.

can be neglected, photo-oxidation takes place within a single cage: i.e. it is formally a unimolecular reaction, uncomplicated by transport of the reactant species to each other. Furthermore, it is a photoreaction, which can be arrested or restarted by switching the radiation off or on. This advantage has opened up new technical possibilities—of studying the kinetics of the variation in reactivity of a substance in the absence of chemical change.

IV. KINETICS OF VARIATION IN REACTIVITY

The first kinetic studies of the variation in the reactivity of molecules located in a solid matrix (Section III) showed[16,17] that the initial reactivity of fused-ring hydrocarbons towards photo-oxidation could be restored by heating the specimens to temperatures 10–30 deg below the glass point of the matrix for a few minutes. This provided estimates of the temperature and time scales required to restore the original reactivity distribution of the molecules.

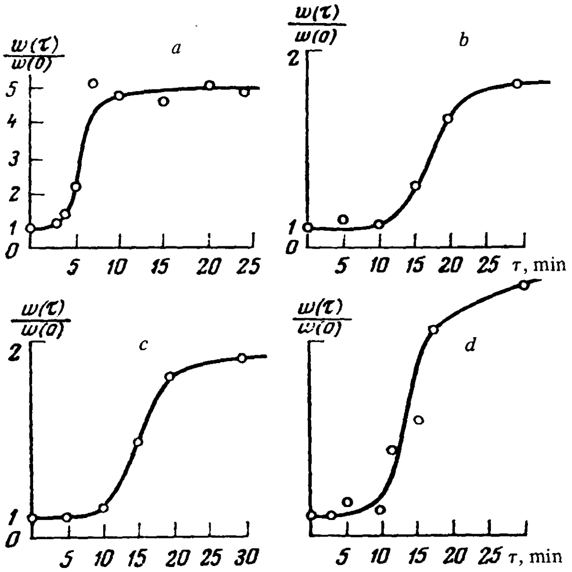


Figure 3. Dependence of relative rate of photo-oxidation $w(\tau)/w(0)$ on duration of thermal activation: *a*) 1.36 mM naphthacene in polystyrene (activated at 70°C, conversion 80%); *b*) 1.36 mM naphthacene in poly(methyl methacrylate) (52°C, 40%); *c*) 5.6 mM anthracene in polystyrene (70°C, 40%); *d*) 3.1 mM naphthacene in polystyrene (60°C, 60%).

In a more detailed study[19] fused-ring hydrocarbons were subjected in polymer films to photo-oxidation at 20°C until a specified degree of conversion was attained. The specimen was then heated in the dark at a fixed temperature T for a certain time τ. After this the specimen was again exposed at 20°C, and the rate of change in the concentration of the oxidisable substance during the second exposure was recorded. The variation in the rate of the process with different times of heating provided a measure of the variation in reactivity of the oxidisable compound during heating. Fig. 3 illustrates the dependence of the relative rate of the second photo-oxidation $W(\tau)/W(0)$ on the time of heating τ at different temperatures. As could have been expected, rise in the temperature of thermal activation accelerates restoration of the equilibrium rate of oxidation; the range of variation in the rate expands with increase in the initial degree of conversion.

A striking feature of Fig. 3 is the sigmoid form of the dependence of rate of photo-oxidation on time of thermal activation at sufficiently high degrees of primary conversion. From simple considerations it might have been expected that maximum rate of change of reactivity would occur with short times of thermal activation, when the reactivity distribution of the species would be most remote from equilibrium. This might have occurred if the change in reactivity had resulted from movement of fluctuations of the free volume through a macroscopically homogeneous specimen[12]. On such a model any molecule can change its reactivity abruptly on thermal activation, passing into a state corresponding to equilibrium. The probability of such a jump is independent of the state of the molecules before thermal activation.

On the other hand, a sigmoid dependence can be observed only if the initial reactivity of the molecule has a significant influence either on the sequence of states through which it passes during thermal activation or on the probability of a change in reactivity. This type of dependence may be expected, for example, if thermal activation involves continuous "diffusion" of molecules from a non-equilibrium to an equilibrium reactivity distribution. We postulate that molecular reactivity χ is determined by a parameter u_1 characterising the state of the molecule in the given medium. Under equilibrium conditions there exists a certain distribution of species according to this parameter $\rho_0(u_1)$. During the first photo-oxidation, when thermal diffusion among states can be neglected, the equilibrium distribution is disturbed by occurrence of the chemical reaction, so that

$$\rho(u_1, t) = \rho_0(u_1)\exp(-\chi(u_1)t), \tag{30}$$

where t is the time of photo-oxidation.

During thermal activation continuous diffusion through states differing in u_1 value will be described by the equation

$$\frac{\partial\rho}{\partial\tau} = D\frac{\partial^2\rho}{\partial u_1^2}, \tag{31}$$

where τ is the time of thermal activation and D the corresponding diffusion coefficient. The boundary conditions for Eqn. (31) correspond to absence of diffusion beyond the extreme values of u_1:

$$\left.\frac{\partial\rho}{\partial u_1}\right|_{u_{1\,\min},\tau} = \left.\frac{\partial\rho}{\partial u_1}\right|_{u_{1\,\max},\tau} = 0. \tag{32}$$

With certain forms of the distribution $\rho_0(u_1)$ the solution of Eqn. (31) enables a sigmoid dependence to be obtained. This occurs, for example, with D constant and independent of u_1, i.e. with the uniform distribution $\rho_0(u_1)$ = const, when

$$\chi(u_1) = -k_0\ln\left(\sin\frac{u_1}{2}\right);\quad 0\leqslant u_1\leqslant\pi, \tag{33}$$

and at degrees of conversion during the first photo-oxidation exceeding 50%.

The above results do not give the reasons for the non-equivalence of reactant species. However, they must be taken into account in constructing models to explain this phenomenon.

V. KINETICS WITH PARTIAL KINETIC NON-EQUIVALENCE OF REACTANT SPECIES

As noted above, under conditions such that the correlation time τ_c of reactant species over all possible states in the medium is intermediate between the time τ_x of significant change in concentration of the reactant species and the lifetime of an active centre τ_e, i.e. when

$$\tau_x \gg \tau_c \gg \tau_e, \tag{34}$$

the variation in macroscopic concentration obeys the usual kinetic laws, while kinetic non-equivalence of the species merely disturbs classical ideas on the relative rates of different possible reactions.

Conditions for such partial kinetic non-equivalence of reactant species can be realised especially easily in photochemical processes. If the light is not too intense, such a process comprises a series of consecutive or parallel physical or chemical changes lasting a relatively short time after absorption of a quantum (usually $\tau_e \ll 1$ s). Each such process usually proceeds until a certain stage is reached, independently of the occurrence of other primary processes initiated by the absorption of other light quanta. Therefore the time τ_e for development of a primary photochemical process is independent of the light intensity. Yet τ_x does depend on the intensity, and usually exceeds τ_e considerably, amounting to minutes, hours, or longer. Evidently, therefore, it is not difficult to find a medium and a photochemical process for which the condition (34) of partial kinetic non-equivalence of reactant species will be satisfied.

A photochemical process can be influenced relatively easily by the introduction of additives that quench excited states. Under conditions of partial kinetic non-equivalence of excited species the intensity of luminescence and the rate of the photochemical process will then vary in different ways.

As example we can consider results for so called unstoppable photochemical processes, which cannot be completely inhibited when the luminescence of the leading species has been extinguished[20]. Phenomena of this type have been known for some time[21,22]. The most common class of photochemical processes involves species in the triplet state, and cannot be completely inhibited by the introduction of quenchers for such states. This is usually explained by the involvement of single excited molecules[23], but this hypothesis is fairly difficult to substantiate. Therefore an alternative explanation of unstoppable processes, based on the kinetic non-equivalence of reactant species, seems quite permissible.

The quenching of excited states by any mechanism can be described approximately by the Stern–Volmer equation[24]: the concentration of molecules in an excited state S^* is

$$[S^*] = \frac{w}{k_d + k_f + k_r + k_q[Q]}, \tag{35}$$

where w is the rate of formation of excited molecules, k_d and k_f are the rate constants of spontaneous and radiative deactivation of excited molecules, k_r is the rate constant of their chemical reaction in the given medium, and k_q is the rate constant of the quenching of S^* by a quencher molecule Q. If, however, the excited molecules are kinetically non-equivalent, Eqn. (35) represents the effect of the quenching agent on the concentration of only one species. Then the total macroscopic concentration of excited species will be described by the integral over all possible local properties that can be effective in the given medium:

$$[S^*] = \int \frac{w\rho(u)\,\mathrm{d}u}{k_d + k_f + k_r + k_q[Q]}, \tag{36}$$

where u is a parameter representing these properties and $\rho(u)$ the density of distribution of concentration with respect to this parameter. In general all the other quantities in (36) are also functions of u.

The quantum efficiencies of luminescence η and of the photochemical process φ will be given by analogous formulae:

$$\eta = \alpha' \int \frac{k_f\rho(u)\,\mathrm{d}u}{k_d + k_f + k_r + k_q[Q]} \tag{37}$$

$$\varphi = \alpha' \int \frac{k_r\rho(u)\,\mathrm{d}u}{k_d + k_f + k_r + k_q[Q]} \tag{38}$$

From these expressions we find that quenchers of excited states have different effects on the intensity of luminescence and on the rate of the photochemical process:

$$\frac{\varphi}{\varphi_0} \neq \frac{\eta}{\eta_0}.$$

Equations (37) and (38) have been subjected[25] to detailed analysis for the case in which the kinetic non-equivalence of the excited molecules is due to the effect of the local properties of the medium on k_r. The character of the $\rho(u)$ distribution is examined by comparing the efficiency of the quenching of luminescence and of the inhibition of the photochemical process by small additions of the quenching agent

$$Z = \left(\frac{\partial(\eta/\eta_0)}{\partial[Q]}\right)_{[Q]=0} \Bigg/ \left(\frac{\partial(\varphi/\varphi_0)}{\partial[Q]}\right)_{[Q]=0} \tag{39}$$

with the type of deviations from the Stern–Volmer equation of the variation of the quantum efficiencies η and φ with the quencher concentration. It was shown that only one of the variations in quantum efficiency—either of the photochemical process or of luminescence—can be expected to diverge considerably from the equation. Quenching agents are always more effective in quenching luminescence than in inhibiting a photochemical process ($Z \leqslant 1$). If a uniform distribution is assumed for the entropy factor S of the chemical reaction rate constant, as is done by many authors in discussing processes with complete kinetic non-equivalence of species (9), considerable deviations from the Stern–Volmer equation appear to be possible only at sufficiently small ratios Z. To explain such departures when Z is large we must postulate other types of distribution, in particular bimodal, based on the presence of two kinds of local conditions, under which excited molecules have significantly different reactivities.

This last hypothesis has been used[28] to explain the effect of oxygen on the photodecomposition and the phosphorescence of benzophenone in poly(methyl methacrylate). Plots of the quantum efficiencies show (Fig. 4) that oxygen is almost twice as effective in quenching phosphorescence as in retarding photodecomposition ($Z \simeq 0.6$), and the Stern–Volmer equation does not describe the inhibition of the photochemical process. These results can be understood on the hypothesis that $\rho(u)$ is bimodal: the lifetimes of triplet benzophenone molecules corresponding to different local conditions differ more than fourfold; and the probability of chemical reaction for species possessing shorter lifetimes exceeds 0.75, while the probability of formation of such species is ~0.4.

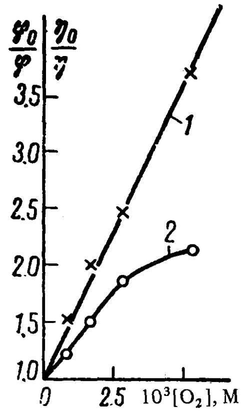


Figure 4. Effect of oxygen on quantum efficiency in 0.29 M benzophenone in poly(methyl methacrylate) exposed to light of wavelength 365 nm and intensity 10^{17} cm^{-2} s^{-1}: 1) phosphorescence; 2) photochemical conversion.

VI. INFLUENCE OF MOBILITY OF MEDIUM ON EFFICIENCY OF PRIMARY CHEMICAL REACTIONS

On passing from liquid-phase systems to solid solutions we find not only the above kinetic features of solid-phase reactions but also a qualitative change in the relative reactivities of species differing in chemical structure. In viscous solutions, especially media that can be regarded as solid, when effective chemical reaction rate constants are remote from diffusion constants, i.e. when encounter between reactant species cannot be the rate-determining stage, a considerable levelling is observed in the activities of chemically different species.

A method for measuring the relative efficiencies with which inhibitors differing in structure act on peroxy-radicals in a solid polymer matrix is based[26,27] on a study of the influence of the inhibitors on the initial rate of consumption of stable quinoline or di-*p*-methoxyphenylnitroxide radicals ($R_{quin}\cdot$ or $R_{dmpn}\cdot$) during initiated oxidation of the polymer. Table 1 shows that the rate constants for interaction of different valency-saturated inhibitors with peroxy-radicals are almost the same in solid polystyrene, whereas they differ hundredfold in the liquid phase. The observed levelling of inhibitor activity cannot be explained by diffusion limiting reaction in the solid phase, with the limiting value of the constant representing the diffusion mobility of the reactants. Such a suggestion is contradicted by the fact that the activity of stable radicals exceeds by factors of 10–20 the "limiting" activity of valency-saturated inhibitors. Since there are no data indicating an abnormally high diffusion coefficient for stable radicals, the result suggests that the levelling effect is not merely a restriction on translational mobility, but has a more complex nature and probably depends on the type of reaction.

Table 1. Effect of polymer matrix on antiradical activity of antioxidants at 70°C.

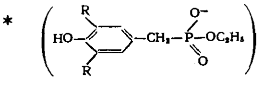
Antioxidant	$10^{-4}k_7$, M^{-1} s^{-1}	
	ethylbenzene	polystyrene*
stable radicals		
$R_{quin}\cdot$	124	51
$R_{dmpn}\cdot$	46	30
valency-saturated inhibitors		
1-Naphthol	44	3.6
Bis-(3-t-butyl-5-methylphenyl)methane-2,2′-diol	41	5.1
Tin thio-2,2′-bis-(4-methyl-6-α-methylbenzylphenol)	20	4.2
Calcium oxide-bis-(3-t-butyl-2-hydroxy-5-methylphenyl)sulphide	18	3.6
Phenylnaphthylamine	13	2.2
Pentaerythritol β-(3,5-di-t-butyl-4-hydroxyphenyl)propionate	4.7	1.9
Bis-(3,5-di-t-butylphenyl)methane-4,4′-diol	2.6	1.5
2,6-Di-t-butyl-4-methylphenol	2.5	2.8
Phenol	0.3	0.3

* Absolute values of the constants determined on the assumption that k_7 for phenol is the same in polystyrene as in ethylbenzene.

Table 2. Change in efficiency of reaction of $^1O_2$ with various compounds on passing from the liquid phase to a solid polymer.

Compound	Efficiency of chemical action $10^{-3}k_r/k_d$, M^{-1}		Efficiency of quenching $10^{-3}k_q/k_d$, M^{-1}		
	CH_2Cl_2	polystyrene	CH_2Cl_2	BMK-5*	polystyrene
β-Carotene	15	0.12	3600	—	8
Nickel dibutyldithiocarbamate	—	—	470	1.3	1.1
Rubrene	9	0.14	—	—	—
Di-*p*-methoxyphenylamine	—	—	9.1	0.5	—
1,2,2,6,6-Pentamethylpiperidine	—	—	7.3	—	0.42
Naphthacene	2.5	0.08	—	—	—
2,4-Xylidine	—	—	3.2	0.2	—
1-Naphthylamine	—	—	2	0.22	—
Bismuth dimethyldithiocarbamate	—	—	1.5	—	0.24
Irgostab 2002**	—	—	0.51	0.19	0.17
Di-*p*-iso-octylphenylamine	—	—	0.12	0.072	—
N-n-Butylphenylnaphth-2-ylamine	—	—	0.041	0.038	—
Anthracene	0.018	0.0037	—	—	—

* A copolymer of methacrylic acid and butyl methacrylate.

**  Ni with R = t-C_4H_9.

$$\left(HO-C_6H_2R_2-CH_2-\overset{O^-}{\underset{O}{P}}-OC_2H_5\right)_2$$

A similar effect has been found for the rate constants in the quenching of singlet oxygen by various substances and its reaction with aromatic hydrocarbons (Table 2).[28-30] Here the levelling is still more clearly defined: in the liquid phase the difference in relative quenching rate constants reaches 10^5, but in the solid it does not exceed factors of 200–300. Such parallel variation in rate constants on passing from the liquid to the solid phase occurs only with reactions of the same type: rate constants for different types of reactions vary differently. Thus the rate constant for reaction between molecular oxygen and rubrene in the liquid phase exceeds those for the quenching of oxygen by almost all substances other than β-carotene and nickel dithiocarbamate, but in solid polystyrene it becomes smaller than those for the action of oxygen on any of the quenching agents investigated. Change in reactivity leading to the levelling effect takes place at temperatures above the glass point of the medium[29]. A study of the efficiency of inhibitors in the thermal oxidation of polyalkenes revealed a levelling phenomenon at temperatures of ~100°C, more than 100 deg above the glass point[31].

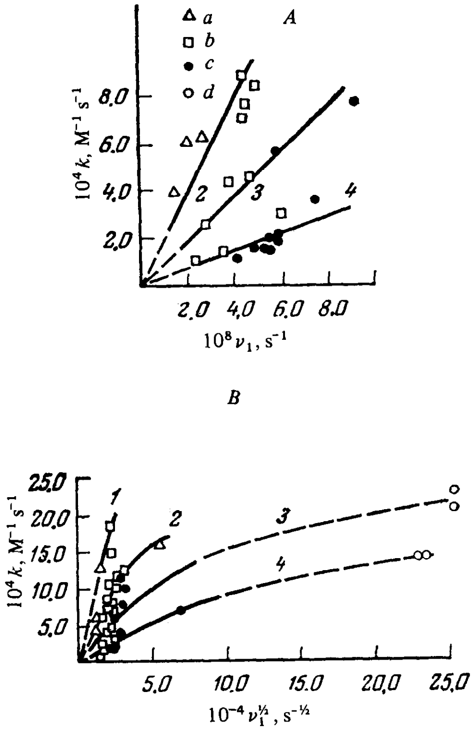


Figure 5. Dependence of rate constant k for reaction of $\rangle$NO with phenol on frequency of rotation of paramagnetic probe: A) at low frequencies; B) over a wide frequency range in various media: a) polystyrene; b) polypropylene; c) polyethylene; d) benzene at different temperatures (°C): 1) 70; 2) 60; 3) 50; 4) 40.

Yet another phenomenon characteristic of reactions in a polymer matrix—the dependence of the reaction rate constant, not limited by diffusion, on the mobility of the medium—has been observed[32-36] in the same matrix at about the same temperature. The reaction of 2,4,6-tri-t-butylphenoxyl with hydroperoxy-groups in polyalkenes exhibits a correlation between its rate constant and the frequency of rotation of a stable nitroxyl radical in the same polymer matrix[32,34]. This correlation was interpreted as due to the effect of the cage on the probability and the rate of change of the mutual orientation of the species in the cage[35]. Rate constants for this reaction[32,34] and for that between the nitroxyl radical 4-benzoyloxy-2,2,6,6-tetramethylpiperidino-oxyl (>NO·) and 2,6-di-t-butylphenol[36] are determined by the change in the frequency of rotation of a paramagnetic probe, and are independent of the nature of the matrix in which the reaction occurs (Fig. 5). Hence the differences in activation energy of these reactions in different media are governed by the difference in the activation energy of rotational mobility in them.

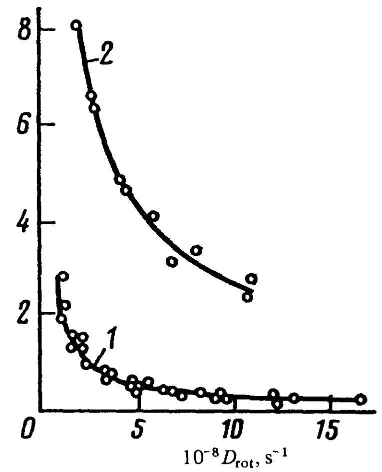


Figure 6. Influence of mobility of medium on ratio of times of translational and rotational diffusion ($n = \tau_{rot}/\tau_{tr}$, with $\tau_{tr} = x/2D_{tr}$ (x = 5 Å) and $\tau_{rot} = 1/6D_{rot}$, where x is the translational displacement of the probe, and D_{tr} and D_{rot} are the coefficients of translational and rotational diffusion) in rubbers at different temperatures: 1) polyenes; 2) polybutyl rubbers.

Both phenomena—levelling of the activity of structurally different species involved in reactions of the same class and the effect of the mobility of the medium on reactions not limited by diffusion—probably have the same origin, change in character of the motion of the species on passing from a liquid to a solid medium. Evidence in support of this suggestion is provided by the fact that the ratio of the correlation time of a paramagnetic probe to the characteristic time of its translational mobility increases with the viscosity of the medium (Fig. 6).[37] Increase in viscosity is probably accompanied by an increase in the number of rotations by the molecule relative to the walls before it escapes from the cage. This tends to increase the probability of chemical reaction when the reactant molecules meet. On passing to more viscous media, therefore, we must evidently expect not only a diminished probability of chemical reaction between species due to the diminished mobility of the medium, and hence also a lower probability that particles will meet, but also an increased probability of chemical reaction resulting from the longer lifetime of reactant species in the same cage.

To examine this last suggestion in greater detail we postulate that two molecules A and B meet, assuming for simplicity that B is considerably smaller than A and that their relative motion can be represented as the movement of a point (B) over the surface of a sphere (A). When the point B enters some reactive region of area s on the spherical surface of A, reaction takes place without energy of activation. In the liquid phase the probability of reaction on the collision of A and B will be given by the ratio of s to the whole spherical surface area S_0, so that the rate constant of this reaction k_{liq} is related to the encounter rate constant $(k_D)_{\mathrm{liq}}$ by the equation

$$k_{\mathrm{liq}} = (k_D)_{\mathrm{liq}}\,\frac{s}{S_0}\,. \tag{40}$$

In the solid phase the probability of reaction in an encounter P_{sd} is increased by movement of the point on the spherical surface during the lifetime of the pair. If $s \ll S_0$ and the path L traversed by the point on the surface is not too long, this probability will be given by the formula

$$P_{\mathrm{sd}} = \frac{s}{S_0} + \frac{L}{\chi\sqrt{s}}\cdot\frac{s}{S_0}\,, \tag{41}$$

in which χ is a coefficient around unity, whose value depends on the configuration of the reactive region.

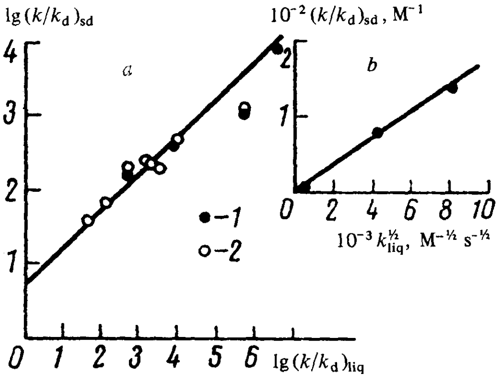


Figure 7. Comparison of rate constants for processes occurring in liquid and solid phases (k_{liq} in methylene dichloride and k_{sd} in: 1) polystyrene; 2) BMK-5: *a*) quenching of singlet oxygen; *b*) chemical interaction with $^1O_2$.

From Eqn. (40) it is easy to obtain a relation between the rate constants of the same reaction in liquid and solid phases:

$$\left(\frac{k}{k_D}\right)_{\mathrm{sd}} = \left(\frac{k}{k_D}\right)_{\mathrm{liq}} + \frac{L}{\chi\sqrt{S_0}}\left(\frac{k}{k_D}\right)_{\mathrm{liq}}^{1/2}. \tag{42}$$

Since all the arguments have been conducted for a case in which the reaction rate constant is far from diffusion-controlled, the formula simplifies to

$$\left(\frac{k}{k_D}\right)_{\mathrm{sd}} = \varphi\left(\frac{k}{k_D}\right)_{\mathrm{liq}}^{1/2}, \text{where } \varphi = \frac{L}{\chi\sqrt{S_0}}, \tag{43}$$

i.e. the reaction rate constant in the solid phase is proportional to the square root of the rate constant of the corresponding liquid-phase reaction. Fig. 7*a* shows that Eqn.(43) describes satisfactorily the results[30] in Table 2 on the quenching of singlet oxygen by various agents: the formula is satisfied for a variation in the reactivity of quenching agents in the liquid phase by factors $>10^5$.

The above reasoning is consistent also with the reactivities of valency-saturated inhibitors and stable radicals towards peroxy-radicals[26,27] (Fig. 8) and with data on the chemical interaction of singlet oxygen with fused rings[28,29] (Fig. 7*b*).

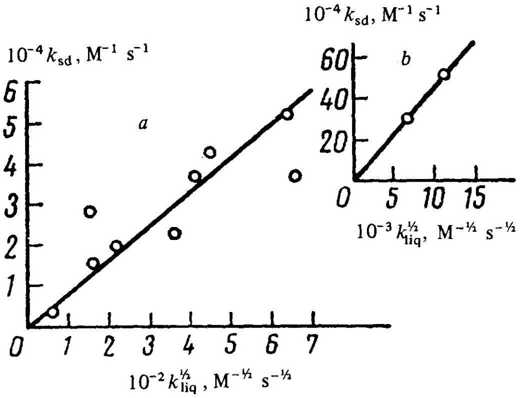


Figure 8. Comparison of rate constants in liquid and solid phases (k_{liq} in ethylbenzene and k_{sd} in polystyrene) for interaction of peroxy-radicals with: *a*) valency-saturated inhibitors; *b*) stable radicals.

The parameter φ has been estimated[30] from the deactivation rate constant k_d and the diffusion coefficient of singlet oxygen. The active centre traverses on the surface of the larger molecule a path of the order of the length of a great circle. This result tends to validate the approximation of a relatively short path made in deducing formula (41).

The models discussed above are evidently extremely rough approximations. However, the experimental results can be explained on the hypothesis that steric factors of the rate constants of chemical reactions in liquid and solid phases are interrelated by the above formulae. The essence of the models is that variation in reactivity is determined by significant change in character of the motion of the reactant species. In the liquid phase this merely involves the meeting or collision of two species; but in the solid phase comparatively lengthy relative motion in the pair is involved.

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It has been thus been shown above that the main kinetic features of solid-phase reactions can be explained in terms of the single concept of a difference between solid and liquid phases in the character of the motion of reactant species in them. Transition from an ideal liquid to an ideal solid involves a sequence of qualitative changes in chemical kinetics. In a relatively mobile medium (at temperatures above the glass point) the relation between the reactivity of chemically different species changes, and their activities level off within a given class of reactions. Roughly under the same conditions the mobility of the medium begins to influence significantly the rate constants of the primary reactions. In more rigid matrices (below the glass point) the relative immobility of the medium does not allow "mixing" of relative species among all possible states in the given medium, which entails the appearance of unusual chemical kinetics.

Several aspects of practical importance—the causes of kinetic non-equivalence of species in structurally different cages, the nature of the relation between the kinetics of variation in cage structure and the kinetics of molecular motions of the matrix, the properties of the medium governing the influence of the motion of species in a cage on their reactivity—remain open questions. The last problem is especially important, since there are indications[36] that a transition from "liquid-phase" to "solid-phase" reactivity occurs in polyalkenes at temperatures above 100°C, more than 100 deg above the glass point, and thus under conditions such that the medium can no longer be regarded as a solid but as a very viscous liquid. It is therefore possible that certain kinetic features of solid-phase reactions can be observed even in ordinary liquid-phase processes.

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Thermochemistry of Halogenomethanes

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Data on the thermochemistry of halogenomethanes are surveyed. The most reliable enthalpies of formation of 17 compounds have been selected by analysing the literature results and the "key" values adopted in recent years. The scope of modern methods for the approximate calculation of the enthalpies of formation of halogenomethanes is examined. Values are recommended for the enthalpies of formation of all 70 halogenomethanes and their reliability is estimated.
The bibliography includes 111 references.

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I. INTRODUCTION

The great importance of organic halogeno-compounds in modern chemistry and technology is due to their extensive and rapidly growing applications. Halogenoderivatives of lower aliphatic hydrocarbons, particularly those of methane, occupy an especially important place among such substances.

The thermochemistry of halogenomethanes is of great interest from both theoretical and practical points of view. The theoretical interest is related to the specific influence of the successive introduction of halogen atoms on the energetic properties of the molecule, which is manifested, for example, by unusual thermochemical reactions[1,2]. The practical interest arises primarily from the necessity to carry out thermodynamic calculations for technical purposes.

Nevertheless the thermochemistry of halogenomethanes has been investigated inadequately and the published data for the enthalpies of formation are contradictory[3-9]. This is caused primarily by the difficulty of the experimental determination of the enthalpies of formation of organic halogeno-compounds, particularly polysubstituted compounds[2,5]. Critical analysis of the available data has shown that this is why reliable enthalpies of formation have been obtained experimentally only for a comparatively small number of halogenomethanes. In many cases the results obtained by different investigators or by different methods show appreciable discrepancies and the choice between them is difficult. Frequently, having at their disposal the same set of initial data, different workers selected "best" values differing by 10–15 kcal mol^{-1}.[5,9,10] Another source of the contradictions in the recommended enthalpies of formation is associated with the necessity to employ methods of approximate calculation, because among the 70 halogenomethanes experimental data are available for a comparatively small number of compounds (not more than 20).

Thus using 17 "reference" values of ΔH_f° which they selected, Yudin and Khachkuruzov[5] estimated the enthalpies of formation of other halogenomethanes by approximate methods. A handbook[3] quoted data for 46 compounds based on their investigation, and still constitutes the most complete compilation of thermochemical constants in the field under consideration. Bernstein[9] estimated the enthalpies of formation of 35 compounds having the composition $CH_nCl_mBr_pF_{4-m-n-p}$ by the method which he proposed. However estimates of the enthalpies of formation by approximate methods involve an even greater arbitrary factor than the choice between experimental values. The results of such estimates generally depend both on the selection of "reference" ΔH_f° values and on the choice of the method of estimation. The estimates of the enthalpies of formation of halogenomethanes by Yudin and Khachkuruzov[5] and Bernstein[9] cannot be regarded as successful for certain groups of compounds. Thus Yudin and Khachkuruzov's[5] enthalpies of formation of chlorofluoromethanes (CH_2FCl, $CHFCl_2$, and CHF_2Cl) proved to deviate appreciably from the true values mainly as a result of the incorrect selection of "reference" ΔH_f° values for fluoromethanes (CH_3F, CH_2F_2, and CHF_3) and also owing to a non-critical application of computational methods[10]. The choice of ΔH_f° in Bernstein's paper[9] for CBr_4, which serves as a basis for the calculation of the enthalpies of formation of other bromo-derivatives, gives rise to appreciable doubts.

The handbooks published in recent years[4,7,8,11] contain carefully selected enthalpies of formation of halogenomethanes, but they include only a comparatively small number of results found experimentally.

This review presents a compilation of the enthalpies of formation of all 70 halogenomethanes. Different experimental methods are described concisely and their possibilities are compared; the difficulties arising in the study of this group of compounds and the methods which can be used to overcome them are discussed. The experimental data are analysed and a value is recommended for each substance. The regularities in the enthalpies of formation of halogenomethanes are considered. The literature methods for the approximate calculation of the enthalpies of formation of halogenomethanes and their theoretical foundations are analysed; recommendations are made concerning the use of these methods.

The enthalpies of formation of the 70 halogenomethanes are recommended on the basis of critically selected most reliable available enthalpies of formation (17 values), the complete set of methods of approximate calculation, and the observed regularities in ΔH_f°. All the recommended values of ΔH_f° have been recalculated on the basis of the key data adopted in 1972–1975 by the International CODATA Commission[12,13].

II. METHODS FOR THE DETERMINATION OF THE ENTHALPIES OF FORMATION OF HALOGENOMETHANES

The most general method for determining the enthalpies of formation of solid and liquid organic compounds is based on the measurement of their enthalpies of combustion in oxygen at an elevated pressure[14,15]. This procedure, developed by Berthelot and known as the bomb calorimetric method, is the most reliable for very many organic compounds of comparatively simple combustion ($C_aH_bO_cN_d$), but its application to organic halogeno-compounds involves considerable difficulties, associated mainly with the complex composition of the combustion products and their highly corrosive nature[2,14,15]. These difficulties may be overcome by employing rotating bombs, auxiliary reducing agents (for organic chloro- and bromo-compounds) and other complications and improvements in the method[14,15]. In the determination of the enthalpies of combustion of liquid and solid organic halogeno-compounds an accuracy to within approximately ±0.01–0.02% can be achieved nowadays, which usually corresponds to the determination of the standard enthalpy of formation with an error not exceeding several tenths of kcal mol^{-1}.[14,15] However, this accuracy can be achieved only when many additional conditions are observed; high purity of the test substances, rapid and complete reduction of the free halogens to hydrogen halides, careful analysis of the solution in the bomb calorimeter and of the gaseous reaction products with subsequent application of reliably determined thermal corrections, etc. The actual discrepancies between the results obtained by different workers amount in many instances to several kcal mol^{-1} and the choice between such values is frequently not evident.

The method involving the determination of enthalpies of combustion in a stream of oxygen under a pressure close to atmospheric has been used successfully for gaseous organic compounds[14,16]. The method is applicable to halogeno-derivatives with a low halogen content, as a rule to monohalogeno-derivatives[16]. The determination of the enthalpies of formation of gaseous compounds with a high halogen content or compounds containing different halogens is more difficult. Their enthalpies of formation are sometimes determined by combustion in oxygen in a bomb calorimeter[2,17,18]. In this case careful analysis of the combustion products is necessary, because the combustion of the gases in the bomb does not as a rule go to completion.

The experimental difficulties encountered in the determination of the enthalpies of combustion of halogenomethanes in oxygen led to the development of many new procedures, usually less universal but having definite advantages in the study of individual groups of compounds. In order to determine the ΔH_f° for gas-phase catalytic reactions, Lacher and coworkers designed a novel isothermal calorimeter of the compensation type[14,19,20]. They used it most often to measure the enthalpies of reactions involving addition to a double bond (chlorination, bromination, hydrobromination, etc.). However, in certain cases, the enthalpies of hydrogenation of organic halogeno-compounds with complete or partial substitution of the halogen by hydrogen were determined[21–23]. These studies made it possible to calculate the standard enthalpies of formation of individual halogenoalkanes, particularly halogenomethanes.

The choice of the catalyst and the reaction conditions is very important for the determination of the enthalpies of gas-phase reactions. The reproducibility of the results of measurements is as a rule fairly high (0.1–0.2 kcal mol^{-1}), but in certain cases there are significant discrepancies with data obtained by other methods[16]. Thus the discrepancy for methyl chloride amounts to ~1 kcal mol^{-1} and is probably associated with failure to take into account the systematic errors in the determination of $\Delta H°$ for the catalytic reaction (for example, owing to the insufficient inertness of the catalyst[16]).

In order to determine the enthalpies of formation of chlorofluorocarbons, particularly chlorofluoromethanes, a method[24-30] based on the measurement of the enthalpies of the reactions of these compounds with alkali metals has been used:

$$CF_nCl_{4-n} + 4M \rightarrow C + n\,MF + (4-n)\,MCl\ ; \quad M = Na \text{ or } K. \tag{1}$$

This reaction is initiated by an electric arc, the energy of which must therefore be accurately measured. It usually results in the formation of amorphous highly dispersed carbon. Since the enthalpies of formation of different specimens of amorphous carbon may differ, it is desirable to determine them experimentally for each series of experiments. In order to prevent side reactions, it is very important to make sure that, when reaction (1) is carried out in a calorimeter, the gaseous substance investigated reacts in its entirety[31]. To make sure that the reaction goes to completion and proceeds unambiguously, it is necessary to carry out numerous measurements and analyses: measurement of the residual pressure in the bomb, analysis of the contents of the bomb for fluoride and chloride ions, weighing of the initial gas, weighing of the alkali metal, and determination of the amount of metal which has not reacted. The accuracy of the results is determined ultimately by the accuracy of these measurements and analyses and also by the accuracy of the measurement of the energy of the arc and of the enthalpy of combustion of the carbon. The enthalpies of reactions with alkali metals can be determined only for a limited range of substances. In terms of accuracy, this method is much inferior to the determination of the enthalpies of combustion in oxygen. Its use for chlorofluoromethanes is justified by the fact that more accurate thermochemical procedures are as a rule inapplicable to this group of compounds[31].

Other methods are still more specific. The application of the method of combustion in fluorine, which has been used successfully in recent years to determine the enthalpies of formation of fluorides and certain other classes of compounds, is restricted in the case of halogenomethanes by the need to determine the enthalpy of formation of carbon tetrafluoride[32,33].

The method based on the measurement of the enthalpies of reduction of halogeno-derivatives by lithium tetrahydroaluminate has been used successfully for certain methane derivatives[34]. The reduction is carried out in ethereal solution in the presence of an excess of lithium hydride. Lithium tetrahydroaluminate is regenerated under these conditions and the reaction may be represented by the equation

$$RX + LiH \xrightarrow[\text{in ethereal soln.}]{LiAlH_4} RH + LiX\ , \tag{2}$$

where X is the halogen (bromine or iodine). The enthalpies of formation of LiH, RH, and LiX are known, so that the calculation of the enthalpies of formation of RX presents no difficulties. The method is mainly applicable to monohalogeno-derivatives. In certain cases the enthalpies of formation of halogenomethanes were determined by measuring the enthalpies of their thermal decomposition reactions[17,35]. The enthalpies of formation of certain chlorofluoromethanes have been measured by the method involving explosion in a spherical bomb[37,38]. The last three methods are applicable solely to a small group of substances and has not as yet been adequately investigated. Their use must be accompanied by particularly careful chemical control of the relevant process.

Apart from the procedures described, there exist also calorimetric methods which have been used only in individual and exceptional cases. Their possibilities are briefly described below in connection with the assessment of specific literature data.

Together with direct measurements, the method involving the determination of the enthalpies of reaction from chemical equilibrium data is frequently used in the thermochemistry of halogenomethanes. Measurement of the equilibrium constants makes it possible to calculate the Gibbs free energy of reaction:

$$\Delta G_T^0 = -RT\ln K_p,$$

or the enthalpy of reaction may be calculated from the equation

$$\Delta H_T^0 = -RT\ln K_p + T\Delta S_T^0 . \tag{3}$$

ΔH_T^0 may be calculated from Eqn. (3) by two procedures. Usually ΔH_T^0 is calculated from the temperature dependence of K_p assuming that ΔS_T^0 is constant. On the other hand, when the values of ΔS_T^0 for the given reaction may be calculated by an independent method, it is possible to evaluate ΔH_T^0 directly. The latter method is more accurate, but is applicable only when the entropies of all the reactants are known (for example, have been calculated on the basis of the Third Law of Thermodynamics).

The calculation of the enthalpies of reaction from equilibrium data does not always lead to reliable results. An essential condition for the successful application of this method is a high accuracy of the measurement of K_p, the attainment of equilibrium over the entire temperature range, and the absence of side reactions. This is particularly important in the calculation of ΔH_T^0 from the temperature variation of K_p.

In a series of careful studies in recent years[39-46], undertaken to investigate equilibria involving halogenomethanes, a high accuracy of the measurement of K_p was achieved as a result of the employment of sensitive instruments for the measurements of pressure and concentration and careful investigation of the equilibrium conditions over a wide temperature range. In terms of the accuracy of the calculation of ΔH_T^0, some of these studies can compete successfully with the measurements of ΔH_T^0 by direct calorimetric methods.

Apart from the equilibrium method, other non-calorimetric procedures are sometimes used. Thus enthalpies of formation have been estimated[5] using the results of the experimental determination of the bond dissociation energies (for example, by the electron impact method). However, this method is much less accurate than those described above. The determination of dissociation energies is usually associated with the measurement of the appearance and ionisation potentials and the accuracy of such measurements is comparatively low (see Yudin and Khachkuruzov[5], Table 3). Furthermore, in order to calculate ΔH_f^0 for compounds in terms of the dissociation energy, it is necessary to know the ΔH_f^0 for the groups involved; these values are also as a rule not accurate. For this reason, the calculation of ΔH_f^0 in terms of dissociation energies can be usefully employed only in the absence of more accurate data and only in those cases where even a rough estimate of the thermochemical quantities is sufficient.

III. KEY VALUES AND UNITS OF MEASUREMENT

To ensure the mutual consistency of all the recommended thermochemical data, the single system of key values developed and adopted by the Committee on Data for Science and Technology (CODATA) is used in the present review. In calculating the enthalpies of formation of halogenomethanes, the following key values of ΔH_f°(kcal mol^{-1}) were used: −68.315 ± 0.010 (H_2O, liq.); −94.051 ± 0.031 (CO_2, gas); −80.15 ± 0.16 (F^-_{aq}); −39.933 ± 0.021 (Cl^-_{aq}); −29.039 ± 0.35 (Br^-_{aq}); 7.388 ± 0.026 (Br_2, gas); −8.695 ± 0.041 (HBr, gas); −57.433 ± 0.015 (Na^+_{aq}); −60.271 ± 0.025 (K^+_{aq}); −22.063 ± 0.031 (HCl, gas); 6.30 ± 0.19 (HI, gas); 14.919 ± 0.019 (I_2, gas).[12,13,47] All the values of ΔH_f° quoted in this review refer to the standard states of the substances and 298.15 K.

The most significant difference between the adopted system of key values and those employed in the most widely used handbooks[4,7] consists in the revision of ΔH_f° (F^-_{aq}). The remaining quantities have remained unchanged or have been changed very insignificantly.

In many instances, apart from the quantities listed above, others (enthalpy of evaporation, enthalpy of dilution, etc.) are needed to calculate the enthalpies of formation of halogenomethanes. These auxiliary quantities were taken from handbooks[4,7] and other publications[48,49]. In calculating the enthalpies of reaction from equilibrium constants, revised values of the thermodynamic functions were used[50].

The enthalpies of formation of compounds in the vast majority of thermochemical studies are expressed in kcal mol^{-1}. To facilitate the comparison of the results, these units were used also in the present review. However, the final data in the Table of recommended values are also expressed in kJ mol^{-1}, which corresponds to the International "SI" system of units adopted by the XIth General Conference on Weights and Measures in 1960.[51,52]. These units are related: 1 cal = 4.184 J.[14] The atomic weights were adopted from Ref. 53.

IV. ANALYSIS OF EXPERIMENTAL THERMOCHEMICAL DATA FOR HALOGENOMETHANES AND SELECTION OF RECOMMENDED ENTHALPIES OF FORMATION

Methane

The bibliography of the determinations of the enthalpy of combustion of methane up to 1970 is given by Glushko[4]. Rossini's study[54] is the most accurate. After applying corrections for the adjustment of the gas to the ideal state[55] and for the modification of atomic weights, these data[54] lead to ΔH_f° (CH_4, gas) = −17.88 ± 0.08 kcal mol^{-1}.[3,4] In 1972 Pittam and Pilcher[56] redetermined the enthalpy of combustion of gaseous methane in an improved calorimeter with a burner[16] and obtained ΔH_f° (CH_4, gas) = −17.80 ± 0.10 kcal mol^{-1}. Pittam and Pilcher had at their disposal a purer methane specimen than in Rossini's work, but, since they calibrated the calorimeter on the basis of the heat of combustion of hydrogen, their results depend on the latter. Since the discrepancy between the values in Refs. 54 and 56 is small, it is desirable to adopt the mean as the recommended value of ΔH_f° (CH_4, gas), i.e.

$$\Delta H_f^\circ(CH_4, \text{gas}) = -17.85 \pm 0.06 \text{ kcal mol}^{-1}.$$

Difluoromethane

Neugebauer and Margrave[57] determined the enthalpy of combustion of difluoromethane in a rotating bomb calorimeter. Since the solubilities and heats of solution of CO_2 and O_2 in HF solution were unknown, the calorimeter was calibrated in three series of experiments: under standardised conditions, with the bomb containing 50 cm^3 of water, and with the bomb containing 50 cm^3 of the HF solution. This procedure enabled the authors[57] to apply a correction for the standard state and also to exclude a secondary thermal effect associated with the corrosion of the walls of the bomb. Mass-spectrometric analysis of the combustion products showed that no substance other than CO_2 and HF were obtained on combustion. Only a small amount of uncombusted difluoromethane was detected. The enthalpy of combustion of CH_2F_2 via the reaction

$$CH_2F_2(\text{gas}) + O_2(\text{gas}) \rightarrow CO_2(\text{gas}) + 2HF \text{ (soln; 2.4 } N)$$

which the present author calculated from the results of individual experiments quoted by Neugebauer and Margrave[57], is −139.83 ± 0.20 kcal mol^{-1}. ΔH_f° (CH_2F_2, gas) = −108.09 ± 0.42 kcal mol^{-1} corresponds to this value.

Trifluoromethane

Neugebauer and Margrave[57] determined the enthalpy of combustion of CHF_3 by the same method as for CH_2F_2 (see above). Their results lead to the following value when account is taken of the key quantities adopted above: ΔH_f° (CHF_3, gas) = −166.47 ± 0.90 kcal mol^{-1}.

The equilibrium in the reaction

$$Br_2 + CHF_3 \rightleftarrows HBr + CBrF_3 \qquad (4)$$

has been investigated[42,58]. Calculation based on the Third Law of Thermodynamics using revised values of thermodynamic functions[50] yielded $\Delta H^\circ(4)$ = −4.26 ± 0.11 kcal mol^{-1} for this reaction. Coomber and Whittle[41] also investigated the equilibrium in the reaction

$$C_2F_6 + Br_2 \rightleftarrows 2CF_3Br \qquad (5)$$

and their results lead to $\Delta H^\circ(5)$ = 3.287 ± 0.075 kcal mol^{-1}.

The equilibria in reactions (4) and (5) were attained from both directions. The results of the measurement of $\Delta H(4)$ and $\Delta H(5)$ make it possible to establish the relation $\Delta H_f^\circ(C_2F_6) - 2\Delta H_f^\circ(CHF_3)$ = 12.193 ± 1.2 kcal mol^{-1}, whence, using $\Delta H_f^\circ(C_2F_6$, gas) = −321.03 ± 1.30 kcal mol^{-1},[50] we obtain ΔH_f° (CHF_3, gas) = −166.97 ± 0.90 kcal mol^{-1}.

The values of ΔH_f° obtained by the two different methods agree within the limits of experimental error. The recommended value is the weighted mean of those quoted above:

$$\Delta H_f^\circ(CHF_3, \text{gas}) = -166.72 \pm 0.64 \text{ kcal mol}^{-1}.$$

Carbon Tetrafluoride

The example of CF_4 shows particularly clearly how difficult is a reliable determination of the enthalpies of formation of organic halogeno-compounds with a high halogen content. In the 15 studies carried out during the period between 1933 and 1965 different methods were used to determine ΔH_f°: combustion of carbon in fluoride[59,60], combustion of methane in fluorine[61], reaction between CF_4 and potassium[24,25] and sodium[27], thermal decomposition of tetrafluoroethylene[17,35], combustion of polytetrafluoroethylene[62,63] and docosafluorobicyclohexyl[64] in oxygen under conditions leading to markedly different CF_4 contents in the combustion product, explosion in a spherical bomb[37,38], etc. However, the results were not very accurate and the maximum discrepancy between them reached more than 70 kcal mol^{-1} (the results range from -162 kcal mol^{-1} [59] to -235 kcal mol^{-1} [24]).

The most reliable results were obtained in recent years by the direct measurement of the enthalpy of fluorination of graphite[32,33]. Domalski and Armstrong[32] combusted a mixture of graphite and Teflon in fluorine. Greenberg and Hubbard[33] achieved a high degree of combustion of graphite by a successful choice of the reaction initiator (silicon powder). The combustion products were carefully analysed in both cases; the amounts of the C_2F_6 and C_3F_8 admixtures in the products were very small and the values of $\Delta H_f^\circ(CF_4$, gas) obtained agree extremely well: -222.87 ± 0.38 kcal mol^{-1} [32] and -223.05 ± 0.20 kcal mol^{-1}.[33] Similar results were also obtained[65] from the measurement of the heat of combustion of Teflon in fluorine: $\Delta H_f^\circ(CF_4$, gas) = -222.0 kcal mol^{-1}, and from a determination[66] of the enthalpy of reaction between dicyanogen and nitrogen trifluoride: $\Delta H_f^\circ(CF_4$, gas) = -223.23 ± 0.5 kcal mol^{-1}. The following value has been adopted[4] on the basis of the results in Refs. 32 and 33:

$$\Delta H_f^\circ(\mathrm{CF_4, gas}) = -223.0 \pm 0.4 \text{ kcal mol}^{-1},$$

This is a key value in the thermochemistry of organic fluoro-compounds and one of the most reliable among the known enthalpies of formation of halogenomethanes.

Chloromethane

The enthalpy of combustion of gaseous chloromethane was determined by Berthelot[67] and Thomsen[68], but the accuracy of their results is low. The enthalpy of the hydrogenation of CH_3Cl to methane was determined in later investigations[21-23], the results leading to $\Delta H_f^\circ(CH_3Cl$, gas) = -20.6 kcal mol^{-1}.[4] Very similar values of ΔH_f° were obtained in a number of compilations[3,6,8] from the results in Refs. 21 and 22. Somewhat later Fletcher and Pilcher[69] determined the enthalpy of combustion of chloromethane in a calorimeter with a heater. Their results lead to the following value:

$$\Delta H_f^\circ(\mathrm{CH_3Cl, gas}) = -19.58 \pm 0.16 \text{ kcal mol}^{-1},$$

which we recommend bearing in mind the reliability of the apparatus and method used[69]. A similar value, ΔH_f°.(CH$_3$Cl, gas) = -19.32 kcal mol^{-1}, was adopted in Ref. 7.

Dichloromethane

The determination of the enthalpy of combustion of CH_2Cl_2 by Berthelot and Ogier[70] is only of historical interest. Smith et al.[71] determined the enthalpy of combustion of CH_2Cl_2 in a stationery bomb calorimeter. Their value of ΔH_c°, adjusted to 25°C, corresponds to ΔH_f°.(CH$_2$Cl$_2$, liq.) = -28.74 kcal mol^{-1}. Taking into account the enthalpy of evaporation, which is 6.90 ± 0.03 kcal mol^{-1},[4] we find $\Delta H_f^\circ(CH_2Cl_2$, gas) = -21.84 kcal mol^{-1}. Lacher et al.[72] measured the enthalpy of the gas-phase hydrogenation of dichloromethane to methane and hydrogen chloride at 250°C. After adjustment to 25°C, their data leads to $\Delta H_f^\circ((CH_2Cl_2$, gas) = -22.92 kcal mol^{-1}. Hu and Sinke[73] redetermined in 1969 the enthalpy of combustion of liquid dichloromethane using a rotating bomb calorimeter and a very pure CH_2Cl_2 specimen. Their results yield $\Delta H_f^\circ(CH_2Cl_2$, liq.) = -29.66 ± 0.07 kcal mol^{-1} or $\Delta H_f^\circ(CH_2Cl_2$, gas) = -22.76 ± 0.08 kcal mol^{-1}. The last value is the most reliable and agrees very well with the data of Lacher et al.[72].

Trichloromethane

The accuracy of the determinations of the enthalpy of combustion of trichloromethane in Refs. 68, 74, and 75 is not high. The data of Smith et al.[71] for the enthalpy of combustion of $CHCl_3$ lead to $\Delta H_f^\circ(CHCl_3$, liq.) = -31.65 kcal mol^{-1} after adjustment to 25°C. Kirkbride[76] measured the enthalpy of the reaction between liquid trichloromethane and gaseous chlorine and his result makes it possible to establish only the relation $\Delta H_f^\circ(CHCl_3$, liq.) = $\Delta H_f^\circ(CCl_4$, liq.) + 0.24 kcal mol^{-1}. The most reliable data are those of Hu and Sinke[73], who determined the enthalpy of combustion of an extremely pure trichloromethane specimen in a rotating bomb calorimeter. Their results[73] lead to $\Delta H_f^\circ(CHCl_3$, liq.) = -32.04 ± 0.35 kcal mol^{-1} or, taking into account $\Delta H_{v298.15}^\circ(CHCl_3$, liq.) = 7.5 ± 0.1 kcal mol^{-1},[4] to $\Delta H_f^\circ(CHCl_3$, gas) = -24.54 ± 0.37 kcal mol^{-1}.

Carbon Tetrachloride

The determination of the enthalpy of combustion carried out by Berthelot[74] and Thomsen[68] are less accurate than the values obtained in later studies. Bodenstein et al.[77] determined the enthalpy of the gas-phase reaction of CCl_4 with hydrogen involving the formation of hydrogen chloride and amorphous carbon. ΔH_f° for amorphous carbon may vary appreciably; having adopted its value from the paper of Neugebauer and Margrave[17], Yudin and Khachkuruzov[5] obtained the following value from the data of Bodenstein et al.[77]: $\Delta H_f^\circ(CCl_4$, gas) = -24.7 kcal mol^{-1}. Baibuz and Medvedev[37,38] found $\Delta H_f^\circ(CCl_4$, gas) = -24.6 ± 1.9 kcal mol^{-1} by an explosion method. Neugebauer[78] measured the enthalpy of the reaction of carbon tetrachloride with magnesium and obtained $\Delta H_f^\circ(CCl_4$, liq.) = -32.3 ± 1.5 kcal mol^{-1}. Smith et al.[71] determined the enthalpy of combustion of CCl_4 in oxygen in the presence of a large amount of an auxiliary substance—only 4% of the measured heat corresponded to CCl_4. After adjustment to 25°C, their data lead to $\Delta H_f^\circ(CCl_4$, liq.) = -29.03 kcal mol^{-1}. Lord and Pritchard[79] studied the equilibrium

$$\mathrm{CO_2(gas) + CCl_4(gas) \rightarrow 2COCl_2(gas)} \qquad (6)$$

and found $\Delta H_{298}^\circ(6) = 16.8 \pm 0.5$ kcal mol^{-1}. Depending on the enthalpy of formation of phosgene adopted, this value leads to $\Delta H_f^\circ(CCl_4$, gas) = -29.75 ± 1.1 or $\Delta H_f^\circ(CCl_4$, gas) = -27.4 ± 0.7 kcal mol^{-1}. In their study of the equilibrium

$$\mathrm{Br_2 + CCl_4 \rightleftarrows BrCl + CBrCl_3,} \qquad (7)$$

Mendenhall et al.[43] obtained $\Delta H^\circ_{298}(7) = 8.84 \pm 0.3$ kcal mol^{-1}; recalculation of this value using revised thermodynamic functions[50] yields $\Delta H^\circ_{298}(7) = 8.37 \pm 0.30$ kcal mol^{-1}. Sullivan and Davidson[80] found $\Delta H^\circ_{298}(8) = -1.44 \pm 0.10$ kcal mol^{-1} for the reaction

$$Br_2 + CHCl_3 \rightleftarrows HBr + CBrCl_3 \quad , \qquad (8)$$

which, together with the previous result, yields the difference $\Delta H^\circ_f(CCl_4, \text{gas}) - \Delta H^\circ_f(CHCl_3, \text{gas}) = 2.44 \pm 0.35$ kcal mol^{-1}. Using the value $\Delta H^\circ_f(CHCl_3, \text{gas}) = -24.54 \pm 0.37$ kcal mol^{-1} adopted above, we obtain $\Delta H^\circ_f(CCl_4, \text{gas}) = -22.10 \pm 0.51$ kcal mol^{-1}.

The most reliable study is that of Hu and Sinke[73], who determined ΔH° for the combustion of a pure carbon tetrachloride specimen in a rotating bomb calorimeter. Their data lead to $\Delta H^\circ_f(CCl_4, \text{liq.}) = -30.61 \pm 0.16$ kcal mol^{-1} or, taking into account the enthalpy of evaporation $\Delta H^\circ_{V298.15}(CCl_4, \text{liq.}) = 7.75 \pm 0.01$ kcal mol^{-1},[4] the result is $\Delta H^\circ_f(CCl_4, \text{gas}) = -22.86 \pm 0.16$ kcal mol^{-1}.

Chlorotrifluoromethane

The values of $\Delta H^\circ_f(CF_3Cl, \text{gas})$ calculated from ΔH° for the reactions of CF_3Cl with potassium[25,26] or sodium[29,30] diverge appreciably: -176.2 kcal mol^{-1} [25]; -167.0 kcal mol^{-1} [26]; -176.7 kcal mol^{-1}.[29,30] These discrepancies are probably a consequence of numerous complications arising in the determination of the heats of reaction with alkali metals (see above). Mears and Stahl's measurements[81] of the enthalpy of the disproportionation reaction lead to -20.85 kcal mol^{-1} for the reaction

$$3HF + CCl_4 \rightarrow CF_3Cl + 3HCl$$

at 573 K, which on recalculation yields $\Delta H^\circ_f(CF_3Cl, \text{gas}) = -172.6$ kcal mol^{-1}. Baibuz and Medvedev[37,38] found $\Delta H^\circ_f(CF_3Cl, \text{gas}) = -167.7 \pm 2.2$ kcal mol^{-1} by an explosion method in a spherical bomb. Lord and coworkers[82,83] studied the equilibria

$$CF_3Cl + I_2 \rightleftarrows CF_3I + ICl \quad , \qquad (9)$$

$$CF_3H + I_2 \rightleftarrows CF_3I + HI \quad . \qquad (10)$$

When revised thermodynamic functions[80] are used, their data lead to $\Delta H^\circ_{298}(9) = 17.22 \pm 0.11$ kcal mol^{-1} and $\Delta H^\circ_{298}(10) = 17.29 \pm 0.15$ kcal mol^{-1}.[82] Hence we obtain $\Delta(\Delta H) = \Delta H^\circ_f(CF_3Cl, \text{gas}) - \Delta H^\circ_f(CF_3H, \text{gas}) = -2.07 \pm 0.30$ kcal mol^{-1}. The quantity $\Delta(\Delta H)$ may also be calculated from Coomber and Whittle's data[42,84] for the equilibria

$$CF_3Br + Cl_2 \rightleftarrows CF_3Cl + BrCl \quad , \qquad (11)$$

$$CF_3Cl + Br_2 \rightleftarrows CF_3Br + BrCl \quad , \qquad (12)$$

$$CF_3H + Br_2 \rightleftarrows CF_3Br + HBr \quad . \qquad (13)$$

They obtained $\Delta H^\circ_{298}(11) = -10.69 \pm 0.30$ kcal mol^{-1}, $\Delta H^\circ_{298}(12) = 10.49 \pm 0.40$ kcal mol^{-1}, and $\Delta H^\circ_{298}(13) = -4.26 \pm 0.11$ kcal mol^{-1}. $\Delta(\Delta H) = -2.75 \pm 0.50$ kcal mol^{-1} when $\Delta H^\circ(11)$ and $\Delta H^\circ(13)$ are used, and $\Delta(\Delta H) = -2.84 \pm 0.53$ kcal mol^{-1} follows from $\Delta H^\circ(12)$ and $\Delta H^\circ(13)$. The average value of the difference $\Delta(\Delta H)$ based on the results in Refs. 42 and 82–84 is -2.55 ± 0.50 kcal mol^{-1}. Since $\Delta H^\circ_f(CHF_3, \text{gas}) = -166.72 \pm 0.64$ kcal mol^{-1}, we obtain

$$\Delta H^\circ_f(CF_3Cl, \text{gas}) = -169.27 \pm 0.81 \text{ kcal mol}^{-1}.$$

Bearing in mind the satisfactory agreement between the three values of $\Delta(\Delta H)$, the last value of the enthalpy of formation appears to be the most reliable.

Dichlorodifluoromethane

The values of $\Delta H^\circ_f(CF_2Cl_2, \text{gas})$ calculated from the ΔH° for the reactions of CF_2Cl_2 with potassium[25,26] or sodium[29,30] agree satisfactorily: -115.6 kcal mol^{-1} [25]; -114.6 kcal mol^{-1} [26]; -115.0 kcal mol^{-1}.[29,30] Mears and Stahl[81] quote $\Delta H^\circ_{573}(14) = -10.97$ kcal mol^{-1} for the reaction

$$2HF + CCl_4 \rightarrow CF_2Cl_2 + 2HCl \, , \qquad (14)$$

which leads to $\Delta H^\circ_f(CF_2Cl_2, \text{gas}) = -119.8$ kcal mol^{-1}. Petersen and Pitzer[85] measured K_p for the reaction

$$2CF_3Cl + CCl_4 \rightleftarrows 3CF_2Cl_2 \quad . \qquad (15)$$

According to their data, $\Delta H^\circ_{298}(15) = 7.64$ kcal mol^{-1} and $\Delta H^\circ_f(CF_2Cl_2, \text{gas}) = -117.9$ kcal mol^{-1}. Mears and Stahl[81] published no information about the experiment and Petersen and Pitzer[85] noted the occurrence of side reactions. We therefore recommend the mean of the three values obtained in Refs. 25, 26, 29, and 30, i.e. $\Delta H^\circ_f(CF_2Cl_2, \text{gas}) = -115.1$ kcal mol^{-1}. The error of this quantity probably does not exceed ± 2 kcal mol^{-1}.

Trichlorofluoromethane

The values of $\Delta H^\circ_f(CFCl_3, \text{gas})$ calculated from the ΔH° for the reaction of $CFCl_3$ with potassium differ significantly: -72.0 kcal mol^{-1} [25] and -64.6 kcal mol^{-1}.[26] Mears and Stahl's data[81] lead to values which vary from -64.7 to -70.2 kcal mol^{-1} depending on the selected method of calculation. Petersen and Pitzer[85] measured K_p for the reaction

$$CF_3Cl + 2CCl_4 \rightleftarrows 3CFCl_3 \, , \qquad (16)$$

and according to their data $\Delta H^\circ_{298}(16) = 10.56$ kcal mol^{-1} and $\Delta H^\circ_f(CFCl_3, \text{gas}) = -68.1$ kcal mol^{-1}. They noted the occurrence of side reactions between chlorofluoromethanes and the catalyst ($AlCl_3$). Baibuz and Medvedev[37,38] found $\Delta H^\circ_f(CFCl_3, \text{gas}) = -67.5$ kcal mol^{-1} by an explosion method in a spherical bomb. Neugebauer[36] measured ΔH° for the reaction of $CFCl_3$ with magnesium and obtained $\Delta H^\circ_f(CFCl_3, \text{gas}) = -66.2$ kcal mol^{-1}. Recalculation of this result on the basis of the system of key quantities adopted in the present review is impossible owing to the lack of information about the experiment in Neugebauer paper[36]. The choice of the recommended value of ΔH°_f is difficult, but the available set of data suggests that it lies in the range between -65 and -70 kcal mol^{-1}. The average value $\Delta H^\circ_f(CFCl_3, \text{gas}) = -67.5 \pm 2.5$ kcal mol^{-1} is recommended.

Bromomethane

Berthelot[67] and Thomsen[68] measured ΔH° for the combustion of bromomethane, but the accuracy of their measurements is low. Bak[86] investigated the equilibrium in the gas-phase reaction

$$CH_3Br + HCl \rightleftarrows CH_3Cl + HBr \tag{17}$$

and $\Delta H^\circ_{298}(17) = -2.41 \pm 0.10$ kcal mol^{-1} and $\Delta H^\circ_f(CH_3Br$, gas) = −8.62 ± 0.19 kcal mol^{-1} were calculated from his data. Hartley et al.[87] determined the enthalpy of the reaction

$$Hg(CH_3)_2(liq.) + 2Br_2(liq.) \rightarrow HgBr_2(cryst.) + 2CH_3Br\ (gas) \tag{18}$$

and found $\Delta H^\circ_{298}(18) = -72.15 \pm 0.61$ kcal mol^{-1}. Together with the ΔH° for the combustion of dimethylmercury,[88] these data lead to $\Delta H^\circ_f(CH_3Br$, gas) = −8.6 kcal mol^{-1}. Fowell et al.[23] determined the enthalpy of the hydrogenation of CH_3Br to methane and their results yield $\Delta H^\circ_f(CH_3Br$, gas) = −8.97 ± 0.34 kcal mol^{-1}.

Adams et al.[89] determined the energy of the reaction of bromomethane with lithium hydride in lithium tetrahydroaluminate, whence they found $\Delta H^\circ_{298}(19) = -3.3 \pm 0.3$ kcal mol^{-1} for the reaction

$$CH_3Br(liq.) + \tfrac{1}{2}H_2(gas) \rightarrow CH_4(gas) + \tfrac{1}{2}Br_2(liq.). \tag{19}$$

We obtain from these data $\Delta H^\circ_f(CH_3Br$, liq.) = −14.55 ± 0.31 kcal mol^{-1} or, taking into account the enthalpy of evaporation $\Delta H^\circ_{V298}(CH_3Br$, liq.) = 5.64 ± 0.10 kcal mol^{-1}, we have $\Delta H^\circ_f(CH_3Br$, gas) = −8.91 ± 0.32 kcal mol^{-1}. Ferguson et al.[90] investigated the equilibrium in the gas-phase bromination of methane with formation of HBr and CH_3Br; calculation from their results based on the Second Law of Thermodynamics yields $\Delta H^\circ_{298} = -8.63$ kcal mol^{-1} for the bromination reaction, while calculation based on the Third Law gives rise to $\Delta H^\circ_{298} = -6.26 \pm 0.10$ kcal mol^{-1}. The latter result corresponds to $\Delta H^\circ_f(CH_3Br$, gas) = −8.03 ± 0.12 kcal mol^{-1}, but conflicts with the results of the majority of other studies. The most probable value is the mean of those obtained in Refs. 23 and 89, i.e. $\Delta H^\circ_f(CH_3Br$, gas) = −8.94 ± 0.30 kcal mol^{-1}.

Bromotrifluoromethane

The enthalpy of reaction (4) and the value of $\Delta H_f(CHF_3$, gas) adopted above lead to $\Delta H^\circ_f(CF_3Br$, gas) = −155.22 ± 0.65 kcal mol^{-1}. Lord et al.[82] investigated the equilibrium

$$CF_3Br + I_2 \rightleftarrows CF_3I + BrI \tag{20}$$

and according to their data $\Delta H^\circ_{298}(20) = 9.55 \pm 0.04$ kcal mol^{-1}. Together with the enthalpy of reaction (10), this yields $\Delta H^\circ_f(CF_3Br$, gas) = −155.55 ± 0.70 kcal mol^{-1}. The following average value is recommended:

$$\Delta H^\circ_f(CF_3Br, gas) = -155.38 \pm 0.65\ kcal\ mol^{-1}.$$

Bromotrichloromethane

Equilibrium (8) was investigated by Sullivan and Davidson[80] and their results made it possible to calculate $\Delta H^\circ_f(CCl_3Br$, gas) = −9.90 ± 0.40 kcal mol^{-1}. The data of Mendenhall et al.[43] for reaction (7) lead to $\Delta H^\circ_f(CCl_3Br$, gas) = −10.65 ± 0.35 kcal mol^{-1}. The mean of the two values quoted, i.e. $\Delta H^\circ_f(CCl_3Br$, gas) = −10.28 ± 0.35 kcal mol^{-1}, may be adopted as the most probable value.

Iodomethane

Berthelot[67,91] and Thomsen[68] measured ΔH° for the combustion of iodomethane, but these studies are only of historical interest. Carson et al.[92,93] determined ΔH° for the reaction of dimethylcadmium with iodine in ether and their results lead to $\Delta H^\circ_f(CH_3I$, liq.) = −3.4 ± 0.8 kcal mol^{-1}.[87] Hartley et al.[87] determined the enthalpy of the reaction

$$Hg(CH_3)_2(liq.) + 2I_2(cryst.) \rightarrow HgI_2(cryst.) + 2CH_3I(liq.) \tag{21}$$

and obtained $\Delta H^\circ_{298}(21) = 44.11 \pm 0.44$ kcal mol^{-1}. These data, together with ΔH° for the combustion of dimethylmercury[88], lead to $\Delta H^\circ_f(CH_3I$, liq.) = −2.3 kcal mol^{-1}. Mackle and Ubbelohde[94] and later Nichol and Ubbelohde[95] measured ΔH° for the reaction of the Grignard reagent with I_2 and HI in solutions in ether and *p*-xylene; the data[95] for the reaction

$$CH_3I(gas) + HI(gas) \rightarrow CH_4(gas) + I_2(gas) \tag{22}$$

lead to $\Delta H^\circ_{291}(22) = -11.04 \pm 1.33$ kcal mol^{-1}, whence it follows that $\Delta H^\circ_f(CH_3I$, gas) = −1.7 kcal mol^{-1}. Carson et al.[34] measured ΔH° for the reduction of iodomethane by lithium tetrahydroaluminate in ether and obtained $\Delta H^\circ_{298}(23) = -15.0 \pm 0.4$ kcal mol^{-1} for the reaction

$$CH_3I(liq.) + \tfrac{1}{2}H_2(gas) \rightarrow CH_4(gas) + \tfrac{1}{2}I_2(cryst.), \tag{23}$$

whence it follows that $\Delta H^\circ_f(CH_3I$, liq.) = −2.85 ± 0.4 kcal mol^{-1}; these are apparently the most accurate measurements for liquid iodomethane.

The most accurate studies on gaseous iodomethane were those of Goy and Pritchard[39] and Golden et al.[40]. They dealt with the equilibrium in the reacton

$$CH_4(gas) + I_2(gas) \rightleftharpoons CH_3I(gas) + HI(gas), \tag{24}$$

and led to $\Delta H^\circ_{298}(24) = 12.61 \pm 0.04$ kcal mol^{-1} [40] and 12.63 ± 0.03 kcal mol^{-1}.[39] These values correspond to $\Delta H^\circ_f(CH_3I$, gas) = 3.38 ± 0.21 kcal mol^{-1} [40] and 3.40 ± 0.21 kcal mol^{-1},[39] which agree very well, but those of Goy and Pritchard[39] are somewhat superior, since the latter investigated a wider temperature range, the reproducibility of the values of K_p was more satisfactory, and the enthalpies ΔH° calculated on the basis of the Second and Third Laws of Thermodynamics agree better. Taking into account the enthalpy of evaporation $\Delta H^\circ_{V298}(CH_3I$, liq.) = 6.6 ± 0.3 kcal mol^{-1}, we obtain $\Delta H^\circ_f(CH_3I$, liq.) = −3.16 ± 0.37 kcal mol^{-1}, in satisfactory agreement with the results of Carson et al.[34] Bearing in mind the difficulty of accurate thermochemical measurements using lithium tetrahydroaluminate, preference must be given to the value of $\Delta H^\circ_f(CH_3I$, liq.), calculated from Goy and Pritchard's data[39] and ΔH°_V.

Di-iodomethane

Berthelot[91] measured ΔH° for the combustion of di-iodomethane and on the basis of his results Glushko[4] obtained $\Delta H^\circ_f(CH_2I_2$, gas) = 28.5 kcal mol^{-1}. More reliable data were obtained by Furuyama et al.[44], who investigated the equilibrium in the reaction

$$2CH_3I \rightleftarrows CH_4 + CH_2I_2 \tag{25}$$

and obtained $\Delta H^\circ_{298}(25) = 4.24 \pm 0.63$ kcal mol^{-1}. This result leads to $\Delta H^\circ_f(CH_2I_2$, gas) = 28.9 ± 0.7 kcal mol^{-1}.

Trifluoroiodomethane

It follows from $\Delta H^\circ_{298}(10)$ that $\Delta H^\circ_f(CF_3I, \text{gas}) = -140.8 \pm 0.7$ kcal mol^{-1}.

V. METHODS FOR THE APPROXIMATE ESTIMATION OF THE ENTHALPIES OF FORMATION OF HALOGENOMETHANES

A whole series of methods have been proposed for the estimation of the enthalpies of formation of organic compounds; a fairly complete bibliography is given in Refs. 96–101. Most of the methods are based on the representation of the energy of formation of the molecule by the sum of the contributions due to its structural elements.

One of the simplest and most widely used additive computational schemes is based on the hypothesis that the average thermochemical bond energies are constant[5,10]. When this procedure is applied to a series of halogenomethanes of the type $CX_{4-n}Y_n$, where X and Y are hydrogen or a halogen, a linear relation between ΔH°_f and n is postulated. Generally speaking, bond energies can vary markedly, particularly in those cases where there is a sharp alteration in the environment of the bond. For this reason, the method of average bond energies as a rule makes it possible to estimate the required quantities only to a rough approximation. This is seen also in relation to certain series of the type $CX_{4-n}Y_n$; thus the experimental enthalpies of formation of compounds of the $CH_{4-n}F_n$ or $CH_{4-n}I_n$ series can be in no way represented by a linear function of n. However, the method of average bond energies may yield entirely satisfactory results when it is used for comparatively small groups of substances of a similar type or for series where the dependence of the bond energies on their environment is believed to be small.

The method proposed by Kharasch[107] also leads to a linear relation between ΔH°_f and n in series of the type $CX_{4-n}Y_n$.[10]

Among the methods where account is taken of the bond environment, only Bernstein's method[9,102], in which account is taken of the interaction of all the atoms, both linked directly and not linked at all, may be widely applied to halogenomethanes. Allowance for pair interactions only leads to a quadratic relation between $\Delta H^\circ_f(CX_{4-n}Y_n)$ and n.[102] On the other hand, the introduction of triple as well as pair interactions leads to a cubic relation[9]. Thus, in order to calculate the enthalpies of formation of compounds in the $CX_{4-n}Y_n$ series, it is necessary to know three[102] or four[9] constants, i.e. to know three or four quantities of the five to be determined.

Other computational schemes taking into account the interactions of bonds or atoms cannot be used owing to the insufficiency of experimental data. Some of these, for example Allen's scheme[98], are used in a few instances to establish relations between the enthalpies of formation of related compounds[103].

Apart from additive schemes, other approximate methods are frequently used, for example, the methods of comparative calculation developed by Karapet'yants[97]. Here it is most convenient to employ the equation

$$F_{II} = AF_I + B, \tag{26}$$

which establishes the relation between the numerical values of the parameter F (for example, ΔH°_f) in two similar series of compounds (I) and (II). The methods of comparative calculation usually yield satisfactory results[97]; in the case of halogenomethanes the greatest difficulty is associated with the selection of the appropriate reference series. Where it is necessary to take into account the structural analogy of the series, the chemical similarity of the fragments by which they differ, and the observed thermochemical regularities (the increase of the C–F bond energy as H is substituted by F,[1,2] the decrease of the C–I bond energy in the analogous substitution, etc.), i.e. series (I) and (II), resembling one another as regards the dependence of ΔH°_f on composition, must be selected.

Estimates of the enthalpies of formation of halogenomethanes by approximate methods are given below. In those cases where the amount of experimental data was sufficient, an additive scheme taking into account the bond environment was used (Bernstein's method[9,102]; Allen's scheme[98,103]). In other cases the ΔH°_f were estimated by methods of comparative calculation[97] using variable reference series, and the method of average bond energies was used for individual small groups of substances.

VI. ESTIMATION OF THE ENTHALPIES OF FORMATION OF HALOGENOMETHANES

Fluoromethanes

No calorimetric determinations have been made for this substance. The accuracy of the mass-spectrometric determinations of $\Delta H^\circ_f(CH_3F, \text{gas})$ in terms of the appearance potential of the CH_3^+ ion or the ionisation potential of the CH_3 radical[104,105] is very low; the results vary from −59 to −79 kcal mol^{-1}.[3]

A more reliable result may be obtained by calculation. Since reliable values of ΔH°_f are available for all the compounds of the $CH_{4-n}F_n$ series except CH_3F, the relevant quantity may be calculated using comparatively accurate computational methods: Allen's scheme[98] and Bernstein's cubic equation[9].

Application of Allen's scheme leads to the relation[103]

$$\Delta H^0_f(CH_3F) = 1/4\,[\Delta H^0_f(CH_4) + \Delta H^0_f(CF_4)] + 3/2\Delta H^0_f(CH_2F_2) - \Delta H^0_f(CHF_3),$$

which yields $\Delta H^\circ_f(CH_3F, \text{gas}) = -55.6$ kcal mol^{-1}. Bernstein's cubic equation gives the same result.

The $CH_{4-n}Br_n$ Series

Reliable values of ΔH°_f are available for CH_4 and CH_3Br in this series. Kaboukov and Perel'man[75] determined ΔH° for the combustion of liquid $CHBr_3$, but their results are very unreliable owing to the incomplete reduction of free bromine, poor reproducibility of the experimental data, and insufficient purity of the specimen.

The difference between the enthalpies of formation of gaseous $CHBr_3$ and CBr_4 may ve calculated from the results of the study of the equilibrium

$$Br_2 + CHBr_3 \rightleftarrows CBr_4 + HBr\ . \tag{27}$$

Strong and Pease[106] obtained $\Delta H^\circ_{298}(27) = -1.0$ kcal mol^{-1} for reaction (27). More accurate measurements[45] lead to $\Delta H^\circ_{298}(27) = -1.66 \pm 0.09$ kcal mol^{-1}. $\Delta H^\circ_f(CBr_4, \text{gas}) - \Delta H^\circ_f(CHBr_3, \text{gas}) = 14.42 \pm 0.10$ kcal mol^{-1} follows from these data.

The available set of data makes it possible to apply Bernstein's quadratic equation, which takes into account the pair interactions between atoms[102], to the calculation of ΔH°_f in the $CH_{4-n}Br_n$ series. The calculation leads to the following values: $\Delta H_f^\circ(CH_2Br_2, \text{gas}) = 1.77$ kcal mol^{-1}, $\Delta H_f^\circ(CHBr_3, \text{gas}) = 14.33$ kcal mol^{-1}, and $\Delta H_f^\circ(CBr_4, \text{gas}) = 28.73$ kcal mol^{-1}. These results are larger than the values adopted in the literature[3,4], because the latter estimates were based on the average bond energies without taking into account the interaction of non-bonded atoms.

The $CH_{4-n}I_n$ Series

The experimental values of ΔH_f° for CH_4, CH_3I, and CH_2I_2 are quoted above. The enthalpy of combustion of crystalline iodoform was determined by Berthelot in 1900[91]; these data were adopted as the basis for the calculation of $\Delta H_f^\circ(CHI_3)$ in a number of compilations[3,4,6,7]. When account is taken of the enthalpies of sublimation, they lead to a value of $\Delta H_f^\circ(CHI_3, \text{gas})$ between 50.3 and 51 kcal mol^{-1}. However, this value appears to be too low: if it is adopted, it is found that the enthalpy of formation varies non-systematically in the $CH_{4-n}I_n$ series and, on passing from CH_2I_2 to CHI_3, the second difference between the ΔH_f° changes sign.

Calculation by Bernstein's quadratic equation[102] using the CH_4, CH_3I, and CH_2I_2 data leads to a significantly different result: $\Delta H_f^\circ(CHI_3, \text{gas}) = 58.7$ kcal mol^{-1}. Analogous calculation for CI_4 yields $\Delta H_f^\circ(CI_4, \text{gas}) = 92.7$ kcal mol^{-1}. The values of $\Delta H_f^\circ(CI_4, \text{gas})$ estimated[3,4] from the average bond energies are approximately 20 kcal mol^{-1} lower. However, comparison of the ΔH_f° data adopted above for CH_4, CH_3I, and CH_2I_2 shows clearly that the dependence of ΔH_f° on n in the $CH_{4-n}I_n$ series is non-linear; for this reason, calculation based on the average bond energies is unjustified in this instance[44].

The $CBr_{4-n}F_n$ Series

Three values of ΔH_f° are known in this series; for CF_4, CF_3Br, and CBr_4 (see above). This makes it possible to use Bernstein's equation[102] for the calculation of the enthalpies of formation of the remaining two compounds. The calculation yields

$$\Delta H_f^\circ(CF_2Br_2, \text{gas}) = -90.9 \text{ kcal mol}^{-1};$$
$$\Delta H_f^\circ(CFBr_3, \text{gas}) = -29.5 \text{ kcal mol}^{-1}.$$

The $CI_{4-n}F_n$ Series

Three values of ΔH_f° are also known in this series: for CF_4, CF_3I, and CI_4. Calculation by Bernstein's equation[102] leads to

$$\Delta H_f^\circ(CF_2I_2, \text{gas}) = -60.8 \text{ kcal mol}^{-1};$$
$$\Delta H_f^\circ(CFI_3, \text{gas}) = 17.0 \text{ kcal mol}^{-1}.$$

The $CBr_{4-n}Cl_n$ Series

Three values of ΔH_f° are known in the CCl_4–CBr series: for CCl_4, CCl_3Br, and CBr_4 (see above). Calculation by Bernstein's equation[102] leads to

$$\Delta H_f^\circ(CCl_2Br_2, \text{gas}) = 2.5 \text{ kcal mol}^{-1};$$
$$\Delta H_f^\circ(CClBr_3, \text{gas}) = 15.5 \text{ kcal mol}^{-1}.$$

The $CCl_{4-n}I_n$ Series

Since only two values of ΔH_f° are known in this series (for CCl_4 and CI_4), it is impossible to estimate the missing quantities by Bernstein's method. They can be estimated from the average bond energies or by the method of comparative calculation[97]. Calculation based on average bond energies yields

$$\Delta H_f^\circ(CCl_3I, \text{gas}) = 6.0 \text{ kcal mol}^{-1};$$
$$\Delta H_f^\circ(CCl_2I_2, \text{gas}) = 34.9 \text{ kcal mol}^{-1};$$
$$\Delta H_f^\circ(CClI_3, \text{gas}) = 63.8 \text{ kcal mol}^{-1}.$$

When the method of comparative calculation is used, it is possible, in principle, to select as a reference any of the eight series of the type $CX_{4-n}Y_n$ examined above; the numerical data obtained for three compounds of the $CCl_{4-n}I_n$ series vary appreciably under these conditions (in the range from 6 to 9 kcal mol^{-1}). The $CH_{4-n}I_n$ and $CH_{4-n}Br_n$ series are probably closest to the $CCl_{4-n}I_n$ series as regards their thermochemical properties. This can be justified as follows: (1) the replacement of an H atom by Cl entails a very small thermochemical effect—thus the first differences between the ΔH_f° in the $CH_{4-n}Cl_n$ series is only approximately 2 kcal mol^{-1}; (2) the non-linear dependence of ΔH_f° on n in the $CH_{4-n}I_n$ and $CH_{4-n}Br_n$ series is probably due to some destabilisation of the compound as the I or Br atoms accumulate (for example, owing to steric hindrance). Presumably this effect also persists in the $CCl_{4-n}I_n$ series. The method of comparative calculation using the $CH_{4-n}I_n$ and $CH_{4-n}Br_n$ series yields very similar results. Data obtained with the aid of the $CH_{4-n}I_n$ reference series are listed below:

$$\Delta H_f^\circ(CCl_3I, \text{gas}) = -0.6 \text{ kcal mol}^{-1};$$
$$\Delta H_f^\circ(CCl_2I_2, \text{gas}) = 26.0 \text{ kcal mol}^{-1};$$
$$\Delta H_f^\circ(CClI_3, \text{gas}) = 57.1 \text{ kcal mol}^{-1}.$$

If a reference series is chosen in which the dependence of ΔH_f° on n is close to linearity, for example $CCl_{4-n}Br_n$, then the result naturally agrees with that calculated from the average bond energies. Since by virtue of the causes mentioned above there are no grounds for the hypothesis that there is a linear relation for the $CCl_{4-n}I_n$ series, preference must be given to the calculation by the comparative method based on the $CH_{4-n}I_n$ series.

The $CBr_{4-n}I_n$ Series

In this series too only two values of ΔH_f° were selected: for CBr_4 and CI_4. The difference between the ΔH_f° for CBr_4 and CI_4 is much smaller than in the case of CCl_4 and CI_4. The choice of a reference series for the calculation of ΔH_f° in the $CBr_{4-n}I_n$ series is therefore less important than in the $CCl_{4-n}I_n$ series. The values of ΔH_f° for the three missing compounds, calculated from the average bond energies and by the comparative method (four reference series), vary in the range of 4 to 5 kcal mol^{-1}. In view of the similarity of the properties of Br and I atoms, the dependence of ΔH_f° on n in the $CBr_{4-n}I_n$ series should presumably be closer to linearity than in the $CH_{4-n}I_n$ and $CH_{4-n}Br_n$ series. The best of the calculated values should therefore lie in the range between those obtained by the Karapet'yants method[97], based on series with a distinct quadratic relation, and those found from the average bond energies. It is useful to employ a reference series in which the quadratic relation is weak, for example $CBr_{4-n}F_n$. Then the method of comparative calculation yields the following data:

$$\Delta H_f^\circ(CBr_3I, gas) = 43.5 \text{ kcal mol}^{-};$$
$$\Delta H_f^\circ(CBr_2I_2, gas) = 59.1 \text{ kcal mol}^{-1};$$
$$\Delta H_f^\circ(CBrI_3, gas) = 75.5 \text{ kcal mol}^{-1}.$$

Chlorofluoromethane, Chlorodifluoromethane, and Dichlorofluoromethane

Among these compounds, experimental data are available only for CHF_2Cl. Edwards and Small[108] investigated the equilibrium

$$2CHF_2Cl \rightleftarrows C_2F_4 + 2HCl \qquad (28)$$

by measuring the pressures of the components at 600°C. They noted the formation of side products and obtained K_p by extrapolation. It follows from their data that $\Delta H_{298}^\circ(28) =$ 28.75 kcal mol^{-1} [11] and $\Delta H_f^\circ(CHF_2Cl, gas) = -115.5$ kcal mol^{-1}. A more reliable value of ΔH_f° may be obtained by the method of comparative calculation based on the $CF_2H_{2-n}Cl_n$ and $CF_{4-n}Cl_n$ (reference) series, where $0 \leqslant n \leqslant 2$:

$$\Delta H_f^\circ(CHF_2Cl, gas) = -111.6 \text{ kcal mol}^{-1}.$$

The compounds CH_2FCl and $CHFCl_2$ may be regarded as members of the $CFH_{3-n}Cl_n$ series, where the enthalpies of formation of the extreme members are known. Calculation by the comparative method using the $CH_{4-n}Cl_n$ reference series (where $0 \leqslant n \leqslant 3$) yields the following results:

$$\Delta H_f^\circ(CH_2FCl, gas) = -58.8 \text{ kcal mol}^{-1};$$
$$\Delta H_f^\circ(CHFCl_2, gas) = -64.7 \text{ kcal mol}^{-1}.$$

In both series considered, $CF_2H_{2-n}Cl_n$ and $CFH_{3-n}Cl_n$, the difference between the values of ΔH_f° for the extreme members of the series is very small, so that the result of the calculation by the comparative method is relatively insensitive to the selection of the reference series. Similar results are also obtained if the constancy of the bond energies in the given series is assumed.

Bromofluoromethane, Bromodifluoromethane, and Dibromofluoromethane

The compounds CH_2BrF and $CHBr_2F$ may be regarded as members of the $CFH_{3-n}Br_n$ series in which the values of ΔH_f° for CFH_3 and $CFBr_3$ are known. Calculation by the comparative method using the $CH_{4-n}Br_n$ reference series (where $0 \leqslant n \leqslant 3$) yields

$$\Delta H_f^\circ(CH_2FBr, gas) = -48.4 \text{ kcal mol}^{-1};$$
$$\Delta H_f^\circ(CHFBr_2, gas) = -39.7 \text{ kcal mol}^{-1}.$$

The value of $\Delta H_f^\circ(CHF_2Br, gas)$ may be obtained by the method of comparative calculation based on the $CF_2H_{2-n}Br_n$ and $CBr_{2-n}F_{2+n}$ (reference) series:

$$\Delta H_f^\circ(CHF_2Br, gas) = -99.7 \text{ kcal mol}^{-1}.$$

Fluoroiodomethane, Difluoroiodomethane, and Fluorodiiodomethane

The choice of the reference series in the calculation of ΔH_f° for the above three substances by the comparative method is particularly important, because the enthalpies of formation of fluoroiodomethanes vary very markedly with composition. Presumably the dependence of ΔH_f° on n for series of the type $CF_{4-m-n}I_nH_m$ with constant m should be close to the variation of these quantities in the $CF_{4-n}I_n$ series. The compounds CHF_2I and $CHFI_2$ may be regarded as members of the $CHF_{3-n}I_n$ series in which the values of ΔH_f° for CHF_3 and CHI_3 are known. Calculation by the comparative method using the $CF_{4-n}I_n$ reference series (where $0 \leqslant n \leqslant 3$) yields

$$\Delta H_f^\circ(CHF_2I, gas) = -89.5 \text{ kcal mol}^{-1};$$
$$\Delta H_f^\circ(CHFI_2, gas) = -14.4 \text{ kcal mol}^{-1}.$$

The value of $\Delta H_f^\circ(CH_2FI, gas)$ may be obtained by the method of comparative calculation involving comparison of the $CH_2F_{2-n}I_n$ and $CF_{4-n}I_n$ (reference) series, where $0 \leqslant n \leqslant 2$:

$$\Delta H_f^\circ(CH_2FI, gas) = -38.7 \text{ kcal mol}^{-1}.$$

Bromochloromethane, Dibromochloromethane, and Bromodichloromethane

By considering the $CBrH_{3-n}Cl_n$ series, in which the values of ΔH_f° for CH_3Br and CCl_3Br are known, and the $CH_{3-n}Cl_{1+n}$ reference series, we obtain

$$\Delta H_f^\circ(CH_2ClBr, gas) = -10.2 \text{ kcal mol}^{-1};$$
$$\Delta H_f^\circ(CHCl_2Br, gas) = -11.0 \text{ kcal mol}^{-1}.$$

The values of ΔH_f° for CH_2Br_2 and CCl_2Br_2 in the $CBr_2H_{2-n}Cl_n$ series are known. Using the $CBr_{4-n}Cl_n$ reference series, where $0 \leqslant n \leqslant 2$, we find

$$\Delta H_f^\circ(CHClBr_2, gas) = 2.1 \text{ kcal mol}^{-1}.$$

We may note that the replacement of H by Cl in the $CBr.H_{3-n}Cl_n$ and $CBr_2H_{2-n}Cl_n$ series entails a very slight change in the values of ΔH_f°. Within the limits of these series, it is possible to use successfully the method of average bond energies; the values of ΔH_f° calculated by this method are very close to those quoted above.

Chloroiodomethane, Dichloroiodomethane, and Chlorodiiodomethane

By considering the $CClH_{3-n}I_n$ series, in which the values of ΔH_f° for CH_3Cl and CI_3Cl are known, and the $CH_{4-n}I_n$ reference series, where $0 \leqslant n \leqslant 3$, we obtain

$$\Delta H_f^\circ(CH_2ClI, gas) = 1.7 \text{ kcal mol}^{-1};$$
$$\Delta H_f^\circ(CHClI_2, gas) = 27.2 \text{ kcal mol}^{-1}.$$

The quantity $\Delta H_f^\circ(CHCl_2I, gas)$ can be readily obtained by considering the $CCl_2H_{2-n}I_n$ series, in which the values of ΔH_f° for CH_2Cl_2 and CI_2Cl_2 are known. Using the $CH_{4-n}I_n$ reference series, where $0 \leqslant n \leqslant 2$, we find

$$\Delta H_f^\circ(CHCl_2I, gas) = -0.6 \text{ kcal mol}^{-1}.$$

In the case under consideration the difference between the enthalpies of formation of the corresponding compounds in the test and reference series is comparatively small (only 2–4 kcal mol^{-1}), which ensures a fairly accurate estimate of ΔH_f° by the comparative method.

Bromoiodomethane, Bromodi-iodomethane, and Dibromoiodomethane

The values of ΔH_f° for $\mathrm{CH_3I}$ and $\mathrm{CBr_3I}$ are known in the $\mathrm{ClH_{3-n}Br_n}$ series. Using the $\mathrm{CH_{3-n}Br_{1+n}}$ reference series, we obtain the following values for $\mathrm{CH_2BrI}$ and $\mathrm{CHBr_2I}$:

$$\Delta H_f^\circ(\mathrm{CH_2BrI, gas}) = 14.8\ \mathrm{kcal\ mol^{-1}};$$
$$\Delta H_f^\circ(\mathrm{CHBr_2I, gas}) = 28.2\ \mathrm{kcal\ mol^{-1}}.$$

The value of $\Delta H_f^\circ(\mathrm{CHBrI_2}$, gas) may be obtained by comparing the $\mathrm{CI_2H_{2-n}Br_n}$ series with the $\mathrm{CH_{2-n}Br_{2+n}}$ reference series:

$$\Delta H_f^\circ(\mathrm{CHBrI_2, gas}) = 43.0\ \mathrm{kcal\ mol^{-1}}.$$

The selection of the reference series for the estimation of the ΔH_f° for the three compounds considered is determined by the similarity of the properties of the Br and I atoms. The latter is manifested particularly in the similarity of the dependence of ΔH_f° on n in the $\mathrm{CH_{4-n}I_n}$ and $\mathrm{CH_{4-n}Br_n}$ series.

Bromochlorodifluoromethane, Bromodichlorofluoromethane, and Dibromochlorofluoromethane

The enthalpies of formation of $\mathrm{CFCl_2Br}$ and $\mathrm{CFClBr_2}$ may be calculated by considering the $\mathrm{CFCl_{3-n}Br_n}$ and $\mathrm{CCl_{4-n}Br_n}$ (reference) series, where $0 \leqslant n \leqslant 3$:

$$\Delta H_f^\circ(\mathrm{CFCl_2Br, gas}) = -55.0\ \mathrm{kcal\ mol^{-1}};$$
$$\Delta H_f^\circ(\mathrm{CFClBr_2, gas}) = -42.4\ \mathrm{kcal\ mol^{-1}}.$$

The value of $\Delta H_f^\circ(\mathrm{CF_2ClBr}$, gas) can be obtained by comparing the $\mathrm{CF_2Cl_{2-n}Br_n}$ series with the $\mathrm{CCl_{4-n}Br_n}$ reference series, where $0 \leqslant n \leqslant 3$:

$$\Delta H_f^\circ(\mathrm{CF_2ClBr, gas}) = -103.1\ \mathrm{kcal\ mol^{-1}}.$$

Similar values of ΔH_f° are obtained, for example, also by considering the $\mathrm{CClF_{3-n}Br_n}$ and $\mathrm{CF_3Br_{1+n}}$ (reference) series or the $\mathrm{CBrF_{3-n}Cl_n}$ and $\mathrm{CF_{4-n}Cl_n}$ (reference) series for $0 \leqslant n \leqslant 3$.

Bromodifluoroiodomethane, Dibromofluoroiodomethane, and Bromofluorodi-iodomethane

By comparing the $\mathrm{ClF_{3-n}Br_n}$ series, in which the values of ΔH_f° for $\mathrm{CF_3I}$ and $\mathrm{CBr_3I}$ are known, with the $\mathrm{CF_{3-n}Br_{1+n}}$ reference series, we obtain:

$$\Delta H_f^\circ(\mathrm{CF_2BrI, gas}) = -76.3\ \mathrm{kcal\ mol^{-1}};$$
$$\Delta H_f^\circ(\mathrm{CFBr_2I, gas}) = -14.8\ \mathrm{kcal\ mol^{-1}}.$$

The value of $\Delta H_f^\circ(\mathrm{CFBrI_2}$, gas) can be obtained by considering the $\mathrm{CI_2F_{2-n}Br_n}$ and $\mathrm{CF_{2-n}BR_{2+n}}$ (reference) series:

$$\Delta H_f^\circ(\mathrm{CFBrI_2, gas}) = 0.7\ \mathrm{kcal\ mol^{-1}}.$$

Similar values of ΔH_f° are obtained also, for example, by comparing the $\mathrm{CBrF_{3-n}I_n}$ and $\mathrm{CF_{3-n}I_{1+n}}$ (reference) series or the $\mathrm{CFBr_{3-n}I_n}$ and $\mathrm{CBr_{4-n}I_n}$ (reference) series, where $0 \leqslant n \leqslant 3$.

Chlorodifluoroiodomethane, Dichlorofluoroiodomethane, and Chlorofluorodi-iodomethane

The values of ΔH_f° for $\mathrm{CF_2ClI}$ and $\mathrm{CFClI_2}$ can be found by considering the $\mathrm{CClF_{3-n}I_n}$ and $\mathrm{CF_{4-n}I_n}$ (reference) series, where $0 \leqslant n \leqslant 3$:

$$\Delta H_f^\circ(\mathrm{CF_2ClI, gas}) = -91.7\ \mathrm{kcal\ mol^{-1}};$$
$$\Delta H_f^\circ(\mathrm{CFlI_2, gas}) = -16.3\ \mathrm{kcal\ mol^{-1}}.$$

Comparison of the $\mathrm{CCl_2F_{2-n}I_n}$ and $\mathrm{CCl_{2+n}F_{2+n}}$ series yields

$$\Delta H_f^\circ(\mathrm{CFCl_2I, gas}) = -42.3\ \mathrm{kcal\ mol^{-1}}.$$

Similar values of ΔH_f° are obtained by comparing other similar series, for example, the $\mathrm{ClF_{3-n}Cl_n}$ and $\mathrm{CF_{4-n}Cl_n}$ (reference) series or the $\mathrm{CFCl_{3-n}I_n}$ and $\mathrm{CCl_{4-n}I_n}$ (reference) series, where $0 \leqslant n \leqslant 3$.

Bromodichloroiodomethane, Dibromochloroiodomethane, and Bromochlorodi-iodomethane

The values of ΔH_f° for $\mathrm{CCl_2BrI}$ and $\mathrm{CClBr_2I}$ are obtained by comparing the $\mathrm{ClCl_{3-n}Br_n}$ and $\mathrm{CCl_{3-n}Br_{1+n}}$ (reference series):

$$\Delta H_f^\circ(\mathrm{CCl_2BrI, gas}) = 13.8\ \mathrm{kcal\ mol^{-1}};$$
$$\Delta H_f^\circ(\mathrm{CClBr_2I, gas}) = 28.5\ \mathrm{kcal\ mol^{-1}}.$$

By comparing the $\mathrm{CI_2Cl_{2-n}Br_n}$ and $\mathrm{CCl_{2-n}Br_{2+n}}$ (reference) series, we find

$$\Delta H_f^\circ(\mathrm{CClBrI_2, gas}) = 42.4\ \mathrm{kcal\ mol^{-1}}.$$

Similar values of ΔH_f° are also obtained by comparing the $\mathrm{ClCl_{3-n}Br_n}$ and $\mathrm{CCl_{4-n}Br_n}$ (reference) series, where $0 \leqslant n \leqslant 3$, or the $\mathrm{CI_2Cl_{2-n}Br_n}$ and $\mathrm{CI_{2+n}Cl_{2-n}}$ (reference) series, where $0 \leqslant n \leqslant 2$.

Bromochlorofluoromethanes

By considering the $\mathrm{CFClH_{2-n}Br_n}$ and $\mathrm{CH_{4-n}Br_n}$ (reference) series, where $0 \leqslant n \leqslant 2$, we find

$$\Delta H_f^\circ(\mathrm{CHFClBr, gas}) = -51.4\ \mathrm{kcal\ mol^{-1}}.$$

A similar value of ΔH_f° (CHFClBr, gas) is obtained by applying the method of average bond energies to the $\mathrm{CFBrH_{2-n}Cl_n}$ series, in which the replacement of H by Cl entails a comparatively small alteration of the enthalpies of formation.

Chlorofluoroiodomethane

Application of the method of comparative calculation to the $\mathrm{CFIH_{2-n}Cl_n}$ and $\mathrm{CH_{4-n}Cl_n}$ (reference) series, where $0 \leqslant n \leqslant 2$, yields

$$\Delta H_f^\circ(\mathrm{CHFClI, gas}) = -40.0\ \mathrm{kcal\ mol^{-1}}.$$

The replacement of an H atom by Cl in the $\mathrm{CFIH_{2-n}Cl_n}$ series entails a comparatively small change in ΔH_f°, so that the result of the calculation of ΔH_f°(CHFClI, gas) depends little on the choice of the reference series. Application of the method of average bond energies to the $\mathrm{CFIH_{2-n}Cl_n}$ series also yields a similar value.

Bromofluoroiodomethane

By considering the $CFIH_{2-n}Br_n$ and $CH_{4-n}Br_n$ (reference) series, where $0 \leqslant n \leqslant 2$, we obtain

$$\Delta H_f^\circ(\mathrm{CHFBrI, gas}) = -27.8\ \mathrm{kcal\ mol^{-1}}.$$

Similar values are obtained using the $ClH_{3-n}Br_n$ or $CFH_{3-n}Br_n$ (for $0 \leqslant n \leqslant 2$) reference series.

Bromochloroiodomethane

The variation of ΔH_f° in the $CBrIH_{2-n}Cl_n$ series is very slight: $\Delta H_f^\circ(CH_2BrI, gas) = 14.8$ kcal mol^{-1} and $\Delta H_f^\circ(CCl_2.BrI, gas) = 13.8$ kcal mol^{-1}. Using the $CBr_2H_{2-n}Cl_n$ reference series, we obtain the following value for the middle member of the series:

$$\Delta H_f^\circ(\mathrm{CHClBrI, gas}) = 14.3\ \mathrm{kcal\ mol^{-1}}.$$

The use of other reference series as well as the method of average bond energies leads to very similar results.

Bromochlorofluoroiodomethane

Comparison of the $CClBrI_{2-n}F_n$ and $CHBrI_{2-n}F_n$ (reference) series leads to the following value:

$$\Delta H_f^\circ(\mathrm{CFClBrI, gas}) = -29.8\ \mathrm{kcal\ mol^{-1}}.$$

In this case the differences between the ΔH_f° for the corresponding members of two similar series are very slight, which improves the reliability of the estimate of ΔH_f° by the comparative method. Similar results are also obtained when other series are used, for example, $CBr.ICl_{2-n}F_n$ and $CI_2Cl_{2-n}F_n$ (reference) series.

VII. CONCLUSION

The recommended enthalpies of formation of all 70 halogenomethanes are listed in the Table. The error of the values chosen as the most reliable experimental data is expressed in terms of 95% confidence intervals (in addition, account was taken of the errors of the determination of all the auxiliary quantities). The only exceptions are CF_2Cl_2 and $CFCl_3$, for which the errors were estimated using the entire set of experimental data obtained and the estimate has no rigorous statistical basis owing to the inadequacy of the experimental methods employed.

The errors of the quantities found by methods of approximate estimation are not quoted in the Table. For the majority of the compounds, they probably do not exceed 3-5 kcal mol^{-1}, which may be supported by the following arguments:

1. The estimates were made by different methods and the discrepancies between the results were comparatively small, as stated above.
2. For certain series of experimental data it was found sufficient to employ additive schemes taking into account the environment of the atoms (Allen's[98] and Bernstein's[9,102] schemes).
3. In calculations by the comparative method, both the test and reference series were varied widely. For each quantity estimated, apart from that quoted in the text, a further 6-8 versions of the calculation were performed; when the series compared were sufficiently "similar", the results differed insignificantly.
4. The calculations by the method of average bond energies were performed only for narrow groups of compounds—mainly in series comprising three members and with a not unduly great variation of the enthalpy of formation. Under such conditions, even estimates carried out by this comparatively rough method could not lead to major errors.

Enthalpies of formation of halogenomethanes.

Compound	$\Delta H^0_{f;\,298,\,15}$ (gas)		Compound	$\Delta H^0_{f;\,298,\,15}$ (gas)	
	kcal mol^{-1}	kJ mol^{-1}		kcal mol^{-1}	kJ mol^{-1}
Experimental data			$CBrI_3$	75.5	315.9
CH_4	−17.85±0.06	−74.68±0.25	CH_2FCl	−58.8	−246.0
CH_2F_2	−108.09±0.42	−452,2±1.8	CHF_2Cl	−111.6	−466.9
CHF_3	−166.72±0.64	−697.6±2.7	$CHFCl_2$	−64.7	−270.7
CF_4	−223,0±0.4	−933.0±1.7	CH_2FBr	−48.4	−202.5
CH_3Cl	−19.58±0.16	−81.9±0,7	CHF_2Br	−99.7	−417.1
CH_2Cl_2	−22.76±0,08	−95,23±0.33	$CHFBr_2$	−39.7	−166.1
$CHCl_3$	−24.54±0.37	−102.7±1.5	CH_2FI	−38.7	−161,9
CCl_4	−22.86±0.16	−95.6±0.7	CHF_2I	−89.5	−374,5
CF_3Cl	−169.27±0.81	−708,2±3.4	$CHFI_2$	−14.4	−60.2
CF_2Cl_2	−115.1±2.0	−481.6±8.4	CH_2ClBr	−10.2	−42.7
$CFCl_3$	−67.5±2,5	−282.4±10.5	$CHCl_2Br$	−11,0	−46.0
CH_3Br	−8.94±0,30	−37.4±1.3	$CHClBr_2$	2.1	8.8
CF_3Br	−155.38±0.65	−650,1±2.7	CH_2ClI	1.7	7.1
CCl_3Br	−10,28±0.35	−43.0±1.5	$CHCl_2I$	−0,6	−2.5
CH_3I	3,40±0,21	14.2±0.9	$CHClI_2$	27,2	113.8
CH_2I_2	28,9±0.7	120.9±2.9	CH_2BrI	14,8	61,9
CF_3I	−140.8±0,7	−589,1±2.9	$CHBr_2I$	28,2	118,0
			$CHBrI_2$	43.0	179,9
Estimated data			CF_2ClBr	−103.1	−431,4
CH_3F	−55.6	−232,6	$CFCl_2Br$	−55.0	−230,1
CH_2Br_2	1.77	7.4	$CFClBr_2$	−42.4	−177,4
$CHBr_3$	14.33	60.0	CF_2ClI	−91.7	−383.4
CBr_4	28.73	120.2	$CFCl_2I$	−42.3	−177,0
CHI_3	58.7	245.6	$CFClI_2$	−16.3	−68.2
CI_4	92,7	387.9	CF_2BrI	−76.3	−319.2
CF_2Br_2	−90.9	−380.3	$CFBr_2I$	−14.8	−61,9
$CFBr_3$	−29.5	−123.4	$CFBrI_2$	0.7	2,9
CF_2I_2	−60.8	−254.4	CCl_2BrI	13.8	57.7
CFI_3	17.0	71.1	$CClBr_2I$	28.5	119.2
CCl_2Br_2	2,5	10.5	$CClBrI_2$	42.4	177.4
$CClBr_3$	15.5	64.9	$CHFClBr$	−51.4	−215.1
CCl_3I	−0.6	−2.5	$CHFClI$	−40,0	−167.4
CCl_2I_3	26.0	108.8	$CHFBrI$	−27.8	−116.3
$CClI_3$	57.1	238.9	$CHClBrI$	14.3	59.8
CBr_3I	43.5	182.0	$CFClBrI$	−29,8	−124.7
CBr_2I_2	59.1	247.3			

However, in certain instances the error of the estimated ΔH_f° may be much greater. This applies particularly to carbon tetraiodide whose enthalpy of formation was obtained by the extrapolation of the experimental data available for the first three numbers of the $CH_{4-n}I_n$ series. Owing to the accumulation of errors, the error in the estimated $\Delta H_f^\circ(CI_4$, gas) may be 10-12 kcal mol^{-1}. For the same reasons, the error in the calculated value of $\Delta H_f^\circ(CBr_4$, gas) may reach 5-6 kcal mol^{-1}. The foregoing applies to a lesser extent to all the tri-iodo- and tribromo-substituted methanes whose enthalpies of formation were estimated.

Although experimental data are available only for a comparatively small number of halogenomethanes and the reliability of the estimated values is limited, nevertheless certain thermochemical regularities are evident for this type of compound. In the first place there is no doubt that in the general case the dependence of the enthalpy of formation of n in series of the type $CX_{4-n}Y_n$ is not linear. For the $CH_{4-n}F_n$ series, an increase of n entails a faster increase of this function compared with the increase that would be expected on the basis of a linear equation. Within the framework of the model of atom—atom interactions, this implies that the bond energies are not constant in the $CH_{4-n}F_n$ series. The additional stabilisation of the molecules arising when the H atoms are replaced successively by F may be associated, for example, with the interaction of fluorine atoms which are not bonded directly[9,102]. Stabilisation as fluorine atoms accumulate is also observed in the $CF_{4-n}Cl_n$, $CF_{4-n}Br$, and $CF_{4-n}I_n$ series, but it is less marked.

In the $CH_{4-n}Cl_n$ series trichloromethane has the maximum absolute enthalpy of formation. Thus in this instance the experimental data cannot be described correctly by any of the proposed computational schemes. Since the experimental enthalpies of formation of all the five compounds in this series are fairly reliable, presumably the computational schemes[9,98,102] take into account inadequately the interaction of the non-bonded atoms. We may note that a similar behaviour is observed also in other organic chloro-compounds, for example, among the chloroethanes investigated the absolute enthalpy is a maximum for 1,1,2,2-tetrachloroethane[4]. It appears that, as the chlorine atoms accumulate at a single carbon atom, the energy of the interaction of the non-bonded atoms does not remain constant; as a result, the slight stabilisation of the chloromethanes which are the first members of the $CH_{4-n}Cl_n$ series is replaced by destabilisation after complete chlorination.

In certain studies it was concluded previously that in the series of halogenomethanes the enthalpy of formation varies linearly with composition[109,110]. This conclusion is a natural consequence of the unsuccessful selection of reference quantities. Papulov and coworkers[109,110] used the most reliable experimental determinations and the data from Glushko's handbook[3] as such quantities; computational methods based on a linear relation were used widely to obtain data of this kind[10].

Analysis of the data obtained by Stull et al.[6] leads to the conclusion that they are frequently mutually contradictory. As an example, it is sufficient to quote the following series[6]:

	CH_2F_2	$CHClF_2$	CCl_2F_2
ΔH_f°, kcal mol	—108.24	— 119.9	—115.0

The contradictory nature of certain numerical data in the above book[6] is due to the fact that the authors used without recalculation a fairly large number of ΔH_f° values obtained by Maslov[111]. The value of $\Delta H_f^\circ(CHClF_2$, gas), which deviates strongly in the above series, was also taken from Maslov's work[111]. Maslov and Maslov[111] estimated ΔH_f° solely on the basis of a simple additive scheme in which the bond energies in all halogenomethanes were assumed to be constant and equal to the bond energies in the tetrahalogeno-derivatives. The choice of reference data in their study[111] is now obsolete and differs strongly from that in the book by Stull et al.[6]

In order to refine further the thermochemical properties of halogenomethanes, it is necessary to increase the number of reliable ΔH_f° reference data. On the one hand, this would make it possible to revise the estimates of ΔH_f° based on the existing computational schemes and, on the other, one could investigate in greater detail the dependence of ΔH_f° for halogenomethanes on composition and the real possibilities of the computational schemes.

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The Interaction of Hydrogen Atoms with Solid Organic Substances

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The mechanisms and kinetics of reactions occurring when solid organic compounds of different structures (low-molecular- and high-molecular-weight substances) are acted upon by "thermal" hydrogen atoms are examined. Models and kinetic schemes proposed for the description of the interaction of solid organic substances with gaseous atomic hydrogen are analysed. The majority of the results summarised in the review refer to the path and rate of the primary chemical step in the interaction. Particular attention has been devoted to reactions of the type $H + RH \rightarrow H_2 + R$, the kinetic constants of which have been measured only in recent years. These data are treated on the basis of the hypothesis of a tunnel mechanism for the transfer of a hydrogen atom at a low temperature. The review also deals with the results of studies of the low-temperature reactions of free radicals with hydrogen atoms and with one another.

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I. INTRODUCTION

The study of the interaction of atomic hydrogen with solid organic substances was initiated in 1958 by Klein and Scheer[1,2], who established that hydrogen atoms add to frozen olefins at a high rate at 77 K. More than 100 studies devoted to the paths and rates of the reactions of atomic hydrogen with solid organic substances have already been published. They are important for the determination of the nature of the elementary steps in the free-radical processes and for the elucidation of the rules relating the structures of the reactants to their reactivities. Furthermore, the study of the reaction of hydrogen atoms with solid organic substances is essential for the understanding of the kinetics and mechanisms of low-temperature chemical reactions as well as heterogeneous processes in systems, frequently encountered in practice, which comprise atomic species in the gas phase and a solid substance.

The knowledge of detailed mechanisms and characteristics of the elementary reactions between the atomic hydrogen and solid organic substances plays a particularly important role in the solution of problems arising in the study of the action of high-energy radiation on such substances. Under the influence of ionising radiation, C–H bonds are ruptured in organic compounds and the reactions of the resulting hydrogen atoms influence the yields of radiolysis products and the radiation stability of the substances.

The reactions of atomic hydrogen with solid organic substances are studied by a wide variety of methods: monitoring of the changes in the pressure of molecular hydrogen, chromatographic or mass-spectrometric analysis of reaction products, and study of the exchange between the gas and solid phases during the interaction of hydrogen isotopes (deuterium and tritium) with frozen hydrocarbons. Lomanov et al.[3] developed the method of kinetic calorimetry for the simultaneous measurement of the heat evolved in the reaction layer and of the amount of hydrogen absorbed. EPR spectroscopy is widely used in the study of reactions of atomic hydrogen with solid organic substances. The free-radical reaction products are identified and their concentration and the concentration of hydrogen atoms are determined by EPR.

Another microwave spectroscopic method is based on the use of a hydrogen maser, the sensitivity of which is higher by approximately 4 orders of magnitude than that of an EPR spectrometer. This makes it possible to investigate reactions in the presence of a very low concentration of atomic hydrogen. It has been suggested[4] that the hydrogen maser be used under pulsed conditions to investigate not only chemical reactions but also the steps preceding them, namely the physical and chemical adsorption of atomic hydrogen on the surface of a solid (from the change in the hyperfine state of the hydrogen atom).

Atomic hydrogen is usually obtained either in the gas phase or is generated directly in the solid substance. The most suitable methods for the generation of atomic hydrogen in the gas phase are thermal decomposition and the dissociation of molecular hydrogen in the gas discharge. The latter procedure is more convenient and effective. The generation of hydrogen atoms in an electrodeless high-frequency or ultrahigh frequency discharge is particularly common. The methods for the generation of hydrogen in the gas phase and the procedures for the measurement of their concentration have been examined in a review[5].

Radiation and photochemical methods are used to generate hydrogen atoms directly in the solid. Among the latter procedures, the method involving the ultraviolet irradiation of frozen aqueous solutions of acids (H_2SO_4 and H_3PO_4) containing small amounts of $FeSO_4$ has come to be most widely used[6,7]. Ultraviolet irradiation of such systems leads to the oxidation-reduction reaction

$$Fe^{2+} + H_2O + h\nu \rightarrow Fe^{3+} + OH^- + H^{\cdot} \quad .$$

The hydrogen atoms produced are stabilised at 77 K, but, on raising the solution temperature to 90–120 K, they become mobile and can react with the solute.

The methods available for the investigation of the interaction of atomic hydrogen with solid organic substances have made it possible to establish fairly reliably the paths of the reactions and in certain cases also to measure their rates. The review presents results referring solely to thermalised hydrogen atoms. The extensive literature on the radiolysis of solid organic substances, from which data for the reactions of atomic hydrogen may be obtained, is not dealt with because radiolysis may entail the formation of "hot" hydrogen atoms.

II. PROCESSES IN SYSTEMS H(GAS) + SOLID ORGANIC SUBSTANCE

1. Models for the Description of Processes

The chemical interaction of hydrogen atoms with organic compounds can be described by the following fundamental equations:

$$\mathrm{M+H} \xrightarrow{k_1} \mathrm{R}, \tag{1}$$

$$\mathrm{RX+H} \xrightarrow{k_2} \mathrm{R+HX}, \tag{2}$$

$$\mathrm{R+H} \xrightarrow{k_3} \mathrm{RH}, \tag{3}$$

$$\mathrm{R+H} \xrightarrow{k_4} {>}\mathrm{C{=}C}{<} + \mathrm{H_2}, \tag{4}$$

$$\mathrm{R+R} \xrightarrow{k_5} \mathrm{R{-}R}, \tag{5}$$

$$\mathrm{R+R} \xrightarrow{k_6} {>}\mathrm{C{=}C}{<} + \mathrm{RH}, \tag{6}$$

$$\mathrm{H+H} \xrightarrow{k_7} \mathrm{H_2}, \tag{7}$$

where M and RX are molecules of unsaturated and saturated compounds respectively. Depending on the structure of the initial molecules, the primary step in the interaction is either the addition reaction (1) or reaction (2) involving the abstraction of an atom or groups of atoms. The transfer of a hydrogen atom (X = H) constitutes a special case of reactions of the second type. For certain compounds with complex structures, there is a possibility of the simultaneous occurrence of reactions (1) and (2) (see Section III). The free radicals generated in the primary step react further with hydrogen atoms [reactions (3) and (4)] and with one another [reactions (5) and (6)]; these secondary reactions of free radicals proceed via recombination [reactions (3) and (5)] or disproportionation [reactions (4) and (6)] mechanisms. Reactions (4) and (6) lead to the formation of molecules with double bonds.

Since the reactant is in the solid phase, physical processes such as diffusion, dissolution or adsorption of hydrogen atoms, and elementary steps involving the migration of the reacting solid-phase species (molecules and free radicals), in the first place their translational diffusion, play an important role in the kinetics. One should also bear in mind that many parameters, for example, diffusion coefficients, may vary as the reaction proceeds, owing to the change in the structure of the initial substance. The fundamental differential equations describing the interaction of hydrogen atoms with an unsaturated compound are presented below [a one-dimensional model is considered; it is assumed that reactions (4) and (6) result in the formation of unsaturated compounds having the same structure as the initial substance]:

$$\frac{\partial [\mathrm{H}]}{\partial \tau} = D_{\mathrm{H}} \frac{\partial^2 [\mathrm{H}]}{\partial x^2} - k_1 [\mathrm{M}] [\mathrm{H}] - (k_3 + k_4) [\mathrm{R}] [\mathrm{H}] - k_7 [\mathrm{H}]^2, \tag{8}$$

$$\frac{\partial [\mathrm{M}]}{\partial \tau} = D_{\mathrm{M}} \frac{\partial^2 [\mathrm{M}]}{\partial x^2} - k_1 [\mathrm{M}] [\mathrm{H}] + k_4 [\mathrm{R}] [\mathrm{H}] + k_6 [\mathrm{R}]^2, \tag{9}$$

$$\frac{\partial [\mathrm{R}]}{\partial \tau} = D_{\mathrm{R}} \frac{\partial^2 [\mathrm{R}]}{\partial x^2} + k_1 [\mathrm{M}] [\mathrm{H}] - (k_3 + k_4) [\mathrm{R}] [\mathrm{H}] - (k_5 + k_6) [\mathrm{R}]^2, \tag{10}$$

where k_1, k_2, k_3, etc. are the rate constants for the above reactions, [H], [M], and [R] are respectively the concentrations of hydrogen atoms, reacting molecules, and free radicals, and D_{H}, D_{M}, and D_{R} are the diffusion coefficients of these species. In the general case the concentrations and diffusion coefficients are functions of the distance x from the surface of the specimen (Fig. 1) and the time τ.

The above equations must be supplemented by the analogous material balance equations for the molecular hydrogenation products (RH and R–R). The solution of the complete system of equations is difficult, but it is quite feasible with the aid of a computer. Thus Rappe et al.[8] calculated on a computer the time variation of the quantity $\partial[\mathrm{H}]/\partial\tau$ for frozen (77 K) isobutene, taking into account reactions (1), (3), (4), (6) and (7), which occur in this system, and the diffusion of all the reacting species (hydrogen atoms, isobutene molecules, isobutyl radicals, isobutane molecules), and in the first version of the calculation it was assumed that the diffusion coefficients are constant throughout the hydrogenation process. The calculated variation of $\partial[\mathrm{H}]/\partial\tau$ with τ agrees with the experimental variation along the initial section; at more advanced stages of the reaction the measured rate decreases faster than would follow from the results of the calculation. In order to account for the discrepancy, the authors suggested that the presence of isobutane leads to a decrease of either (1) the rate of diffusion of hydrogen atoms and of all the solid-phase reacting species or (2) the solubility of hydrogen atoms. When either of these possibilities was taken into account, satisfactory agreement between the experimental and calculated data was achieved. However, one should note that the reaction rate constants and diffusion coefficients used in the calculation have not been measured experimentally in most cases and are not always reliable. For this reason, the results must be treated with a certain amount of caution.

It is seen from the above example that the correct description of the interaction of hydrogen atoms with solid organic substances requires the knowledge of many constants for chemical and physical processes. In practice, in order to simplify the problem, use is made of approximate models. Among all the transport phenomena, commonly only the diffusion of atomic hydrogen is taken into account, while the diffusion of molecules and free radicals is neglected (the H-diffusion model[8-10]).

It is usually assumed that $\partial[\mathrm{H}]/\partial\tau = 0$. Then

$$D_{\mathrm{H}} \frac{\partial^2 [\mathrm{H}]}{\partial x^2} = k_1 [\mathrm{M}] [\mathrm{H}] + k_3 [\mathrm{R}] [\mathrm{H}] + k_4 [\mathrm{R}] [\mathrm{H}] + k_7 [\mathrm{H}]^2. \tag{11}$$

The distribution of the concentration of atomic hydrogen in the layer of the given substance, where a whole series of reactions take place simultaneously, is complex. We shall confine ourselves to an examination of two special cases which are encountered in practice.

(a) The distribution of the concentration of atomic hydrogen determined by the rate of recombination of hydrogen atoms [reaction (7)]. One can state *a priori* that this mechanism should obtain for saturated compounds (such as alkanes) at very low temperatures (< 80 K):

$$D_{\mathrm{H}} \partial^2 [\mathrm{H}]/\partial x^2 = k_7 [\mathrm{H}]^2, \tag{12}$$

$$[\mathrm{H}] = \{[\mathrm{H}]_0^{-1/2} + (k_7/6D_{\mathrm{H}})^{1/2} x\}^{-2}, \tag{13}$$

where $[\mathrm{H}]_0$ is the concentration of atomic hydrogen on the surface of the specimen for $x = 0$.

(b) The consumption of atomic hydrogen is determined by reaction (1) or (2) (depending on the structure of the initial substance). This special case corresponds to compounds reacting with atomic hydrogen at a high rate. These include in the first place unsaturated and many saturated compounds at temperatures ⩾ 100 K (see Section VI). Eqn. (11) transforms into

$$D_H \partial^2 [H]/\partial x^2 = k_1 [M] [H], \tag{14}$$

$$[H] = [H]_0 \{ch (k_1 [M]/D_H)^{1/2} x - th (k_1 [M]/D_H)^{1/2} l \cdot sh (k_1 [M]/D_H)^{1/2} x\}. \tag{15}$$

The measured parameters are usually the rate of change of the pressure of molecular hydrogen (when the reactions proceed in a closed system) and the rate of formation of free radicals. The corresponding equations for the rate of addition are

$$-2 \frac{d H_2}{d \tau} = \int_0^l \{k_1 [M] [H] + (k_3 - k_4) [R] [H]\} s\, d x, \tag{16}$$

$$\frac{d N}{d \tau} = \int_0^l \{k_1 [M] [H] - (k_3 + k_4) [R] [H] - (k_5 + k_6) [R]^2\} s\, d x, \tag{17}$$

where H_2 is the total number of hydrogen molecules in the system, N the number of free radicals in the specimen, s the surface area of the specimen, and l its thickness. On substituting the expressions for [H] [Eqns. (13) and (15)] in these equations, it is possible to obtain the dependence of the rates of the processes on $[H]_0$ and D_H for the two cases considered.

We shall deal with the more interesting case (b). The initial rate of consumption of molecular hydrogen is

$$2 \left(\frac{d H_2}{d \tau}\right)_0 = \int_0^l k_1 [M] [H] s\, d x = (D_H k_1 [M])^{1/2} [H]_0 s\, th (k_1 [M]/D_H)^{1/2} l. \tag{18}$$

It is assumed that $[H]|_{x=0} = [H]_0$ and $\partial[H]/\partial x|_{x=l} = 0$. For a very thin layer, we have

$$-2 \left(\frac{d H_2}{d \tau}\right)_0 = k_1 [H]_0 [M] s l. \tag{19}$$

An analogous expression is obtained for the initial rate of accumulation of free radicals:

$$(d N/d \tau)_0 = k_1 [H]_0 [M] s l. \tag{20}$$

Thus the initial rate of reaction for thin-layer specimens is proportional to their thickness, the concentration of hydrogen atoms, and the concentration of the reactant. For a thick-layer specimen, Eqn. (18) becomes

$$-2 \left(\frac{d H_2}{d \tau}\right)_0 = [H]_0 s (D_H k_1 [M])^{1/2}, \tag{21}$$

i.e. the initial rate of change of the pressure of molecular hydrogen is independent of the thickness of the specimen and is proportional to the concentration of atomic hydrogen and the square root of the concentration of the reactant.

The model involving the diffusion of hydrogen atoms is suitable for the description of the interaction with solid organic compounds, whose molecules have no mobility or their mobility is restricted. For low-molecular-weight compounds, the temperature range in which it is possible to employ the H-diffusion model depends on the melting point (T_m) and usually includes temperatures $T \leqslant T_m/2$. For high-molecular-weight compounds, the upper limit of this temperature range is approximately T_g − 20°, where T_g is the glass point of the amorphous polymer, or is close to the melting point of the crystalline polymer.

The given model is sometimes applicable also to hydrocarbons with a low melting point, such as, for example, propene and isobutene. The foregoing refers to thin films of olefins. Thus it has been found that[8] the initial rate of absorption of molecular hydrogen by isobutene ($l \leqslant 0.5$ m) at 77 K varies linearly with the concentration of atomic hydrogen in the gas phase and with film thickness. The linear dependence of $dH_2/d\tau$ on l has also been observed for propene[9]. For thick films of olefins (~ 1 μm), the rate ceases to depend on film thickness, approaching a constant value[9].

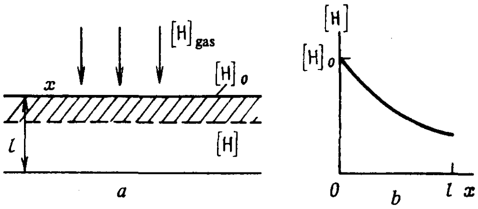


Figure 1. Schematic representation of the interaction of hydrogen atoms (gas) with a solid (*a*) and variation of the concentration of hydrogen atoms in a layer with a thickness l (*b*).

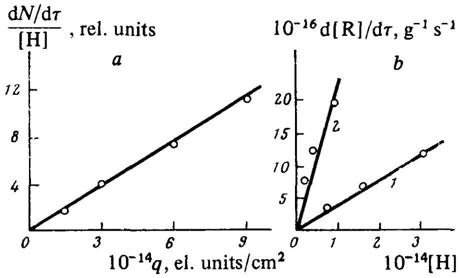


Figure 2. Dependence of the initial rate of formation of free radicals in polyisobutylene adsorbed on aerosil (s_{sp} = 200 m^2 g^{-1}) on the number of elementary units (q) of the polymer (*a*) and the concentration of atomic hydrogen in the gas phase (*b*): *a*) T = 100 K, the number of radicals and the number of elementary units are referred to unit surface of aerosil; *b*) $q = 6 \times 10^{14}$ elementary units per cm^2, T = 115 K (line *1*) and 163 K (line *2*).

However, studies of the interaction of atomic hydrogen with thick propene films established a whole series of facts, which could not be explained within the framework of the H-diffusion model and indicated a high diffusion coefficient of the olefin. It was found that (1) the initial rate of reaction is proportional to [M] and not $[M]^{1/2}$, as would follow from Eqn. (21),[1] (2) the rate depends on the type of matrix in which the olefin is located[11], the consumption of molecules in rigid matrices being proportional to $\tau^{1/2}$ and not τ, and (3) when the hydrogenation is interrupted and the supply of atomic hydrogen is then resumed, the rate of reaction increases significantly[12]. The low concentration of free-radical products of propene and isobutene hydrogenation, which cannot be measured by EPR ($\leqslant 6 \times 10^{17}$ g^{-1}) also constitutes indirect indication of the mobility of olefins. The surface reaction model has been put forward to account for the observed phenomena[8,11]. It is suggested that the reaction proceeds on the surface where the concentration of hydrogen atoms is $[H]_0$, while the concentration within the layer is zero. The model takes into account the diffusion of the reacting substance from the bulk of the layer onto the surface, and it is assumed that the diffusion coefficient is independent of the composition of the layer and the duration of the process. According to the model, the initial rate of absorption of hydrogen is independent of the thickness of the layer and is proportional to the concentration of the reactant and hydrogen atoms:

$$-2\left(\frac{dH_2}{d\tau}\right)_0 = k_1 [H]_0 [M] s \quad . \tag{22}$$

At more advanced stages of the process there is a possibility of two limiting cases where the rate is determined by (a) the chemical reaction [(1) or (2)] on the surface and (b) the diffusion of the reactant. If the rate of the process is limited by that of the reaction, Eqn. (22) is applicable, and, when it is limited by the rate of diffusion, we have

$$\Delta H_2 \simeq (D_M \tau/\pi)^{1/2}. \tag{23}$$

The model agrees satisfactorily with experimental data for thick films at advanced stages in the hydrogenation of propene in different matrices[11].

Systems where the reacting molecules are adsorbed on the surface of an inert carrier constitute the simplest case[13-15]. When such specimens are used, all the reactions take place on the surface and one may disregard the diffusion of hydrogen atoms and the reacting species.

The adsorbent is usually aerosil (SiO_2) with a high specific surface ($\geqslant 200$ m^2 g^{-1}); it is a non-porous fine-grained powder (particle size between 4 and 40 nm), which readily adsorbs organic substances. The specific surfaces of the specimens are the same as the specific surface of the initial aerosil when the adsorbed amounts correspond to approximately 1–2 molecular layers (5–10 μmole m^{-2}). The reaction kinetics may be described by Eqns.(19) and (20), which are valid for a very thin layer of reactant (in this case the average thickness of the layer l corresponds to only 1–2 molecular diameters).

For low surface coverages of aerosil, the amount of free radicals formed varies linearly with the amount of adsorbed polymer (Fig. 2*a*). For high coverages, the linearity breaks down. Fig. 2*b* shows that the initial rate of accumulation of radicals for the polymer adsorbed on a thin layer of aerosil, as well as for olefin films, is proportional to the concentration of hydrogen atoms in the gas phase.

2. The Mechanisms of Elementary Chemical Reactions for Certain Compounds

The compositions of the molecular hydrogenation products have been analysed for the simplest olefins and the mechanisms of chemical reactions leading to hydrogenation have been fairly reliably established[8,9,11,12,16-22]. When propene is acted upon by atomic hydrogen, mainly propane and dimethylbutane are formed. In soft matrices (propene, propene + propane, propene + n-butane), reactions (1), (5), and (6) take place and of the two reactions of isopropyl radicals with each other disproportionation is the dominant process[9,11,20-23]. The rates of reactions (3) and (4) are insignificant, but their role increases in rigid matrices, where the probability of the interaction of free radicals with one another is reduced. Thus in solid mixtures of propene with isopentane[24] and *cis*-butene[11] and in propene adsorbed on quartz[18] isopropyl free radicals are destroyed mainly via reactions (3) and (4).

In order to determine the sequence of the elementary processes occurring in the hydrogenation of olefins, some investigators[21,24-26] studied the deuterium–hydrogen exchange between the gas and solid phases. It was found that, when propene is acted upon (at 77 K) by deuterium atoms, hardly any HD is formed[25]. On the other hand, when butene, isobutene, 2-methylbut-1-ene, and 3-methylbut-1-ene are bombarded by atomic deuterium, H–D exchange takes place at a high rate[25,27]. Its rate for isobutene is close to the rate of absorption of deuterium. The isotope exchange may be caused by the two reactions:

$$R + D \rightarrow \text{olefin} + HD + 60 \text{ kcal mole}^{-1}, \tag{24}$$

$$R + D \rightarrow R_D + H + 0 \text{ kcal mole}^{-1}. \tag{25}$$

Here R_D is a free radical containing a D atom.

The simultaneous study of heat evolution and the amount of absorbed deuterium in the case of isobutene showed[25] that the H–D exchange must be due to a thermally neutral process, i.e. reaction (25). The authors therefore believe[25,27] that the mechanism involving reactions (1)–(7), occurring when solid olefins are acted upon by atomic hydrogen, should be supplemented by the exchange between free radicals and hydrogen atoms. However, the possibility of such an energetically unfavourable process requires further experimental confirmation.

The interaction of atomic hydrogen with many high-molecular-weight [polyisobutylene, polypropylene, poly-(methyl acrylate), etc.] and low-molecular weight (n-hexadecane, malonic acid) compounds at a fairly low temperature may be described by reactions (2)–(4). This conclusion is based on the results of kinetic studies by EPR[14,15,28]. The curves representing the variation of the concentration of free radicals in the substances enumerated above are described by the equation

$$\frac{d[R]}{d\tau} = k_2 [H][RH] - (k_3 + k_4)[H][R]. \tag{26}$$

Similarly the rate of formation of free radicals in unsaturated compounds may be represented by the expression

$$\frac{d[R]}{d\tau} = k_1 [H][M] - (k_3 + k_4)[H][R]. \tag{27}$$

A simultaneous study of the rate of accumulation of free radicals and of the rate of change of pressure in the system makes it possible to determine which of the two reactions [(3) or (4)] predominates. For unsaturated compounds, the rate of absorption of hydrogen is

$$-2\frac{dH_2}{d\tau} = k_1 [H][M] + (k_3 - k_4)[H][R]. \tag{28}$$

Under the conditions of a steady-state concentration of free radicals, we have

$$-\frac{dH_2}{d\tau} = \frac{k_1 k_3}{k_3 + k_4}[H][M]. \tag{29}$$

Two extreme cases are possible:

$$\text{when } k_3 \gg k_4 \qquad -dH_2/d\tau = k_1 [H][M] \, ,$$
$$\text{when } k_3 \ll k_4 \qquad -dH_2/d\tau \approx 0 \, .$$

The nature of the kinetic curves for polystyrene[29] (Fig. 3) shows that in this instance $k_3 \gg k_4$, i.e. the interaction of atomic hydrogen with polystyrene includes only two chemical reactions [(1) and (3)].

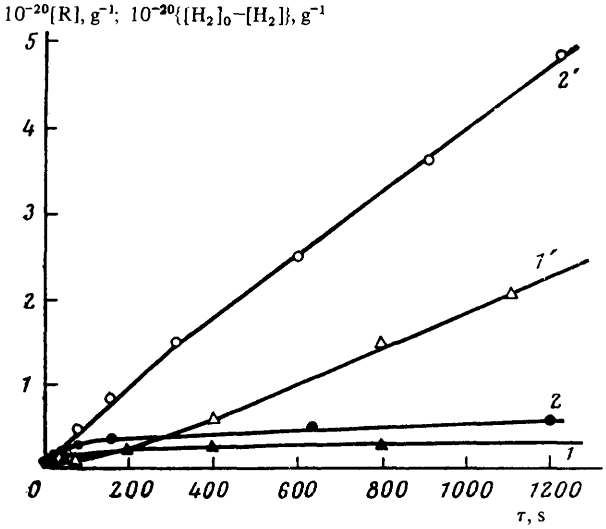


Figure 3. Kinetic curves for the variation of the concentration of free radicals (lines *1* and *2*) and the absorption of molecular hydrogen (lines *1′* and *2′*) in the interaction of atomic hydrogen with polystyrene at 123 K (lines *1* and *1′*) and 163 K (lines *2* and *2′*).[29] The amounts of free radicals and H_2 molecules are referred to unit mass of the polymer.

3. The Depth of Penetration of Hydrogen Atoms into a Layer of a Solid Organic Substance

The relation between the rates of diffusion and chemical reactions in the layer of reactant determines the depth of penetration of atomic hydrogen δ into this substance. Thus δ depends on the chemical structure of the reactants, their physical properties, and, finally, temperature. It can be measured by various experimental methods, including EPR. Since in thick layers hydrogen atoms penetrate only into a layer with a thickness δ, free radicals are likewise formed only in this layer. The average concentration of radicals in such specimens therefore differs from the local concentration in the δ layer: $[R]_{av} = [R]_{loc} s\rho\delta$ (here s is the specific surface of the specimen and ρ its density). Knowing the average and local concentrations of free radicals, it is possible to determine δ. $[R]_{av}$ is measured directly by EPR, while $[R]_{loc}$ is found by studying the broadening of EPR spectra with increasing amount of free radicals, which is due to the dipole–dipole spin interaction. The width of an individual line in the EPR spectrum usually varies linearly with the concentration of radicals (Fig. 4) and $[R]_{loc}$ can be calculated from the equation[30]

$$\Delta H = \Delta H_0 + 5 \cdot 10^{-20} [R]_{loc}, \qquad (30)$$

where ΔH_0 is the intrinsic width of the individual spectral line and ΔH the width of the same line increased owing to the dipole–dipole interaction.

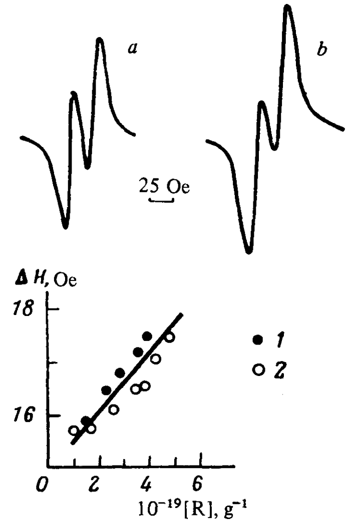


Figure 4. Dependence of the width of an individual line in the EPR spectrum of polyisobutylene radicals on the concentration of the latter[33]. Reaction temperature 145 K (*1*) and 123 K (*2*). The upper part of the figure represents the EPR spectra of free radicals at 145 K. Duration of exposure to the action of hydrogen atoms: *a*) 40 s; *b*) 400 s.

Table 1. The depth of penetration by hydrogen atoms into certain solid organic substances.

Substance	T, K	$10^5\delta$, cm	References
Propane	77	10	1
Propene	77	1—10	1
Propene	77	0.2	27
Polystyrene	295	1	31
Thymine	295	2—3	32
Poly(methyl methacrylate)	100	0.2	33
Poly(vinyl acetate)	120	0.1—0.2	33

Table 1 presents the values of δ for certain organic substances. Those for thymine and poly(methyl methacrylate) were determined by the method described above.

The depth of penetration by atomic hydrogen in solid organic substances of different chemical structures in the temperature range 77–300 K is 10^{-6}–10^{-5} cm (Table 1). Only for propane is δ greater (10^{-4} cm), which can be accounted for by the high rate of diffusion of atomic hydrogen in this substance compared with the rate of destruction of hydrogen atoms on recombination and chemical interaction with propane.

In estimating the values of δ for propene at 77 K the authors of the first investigations[1] did not take into account the possibility of the diffusion of the olefin to the surface of the film, which led to unduly high values of δ. In a later study[11], where an olefin-diffusion model was considered, the estimated δ amounted to only a few molecular diameters.

III. THE PRIMARY CHEMICAL STEP IN THE INTERACTION OF ATOMIC HYDROGEN WITH ORGANIC COMPOUNDS OF DIFFERENT CLASSES

1. The Paths of Reactions (1) and (2)

The path of the chemical reaction can be determined from the EPR spectra of free radicals (Fig. 5) and by analysing molecular products. In most cases the hyperfine structure of EPR spectra is susceptible to elucidation and the directions of reactions (1) and (2) have been established reliably. Since this information is given in a monograph[34] and it is only briefly discussed in the present review, emphasis is laid on the results obtained after the publication of the book by Pshezhetskii et al.[34]

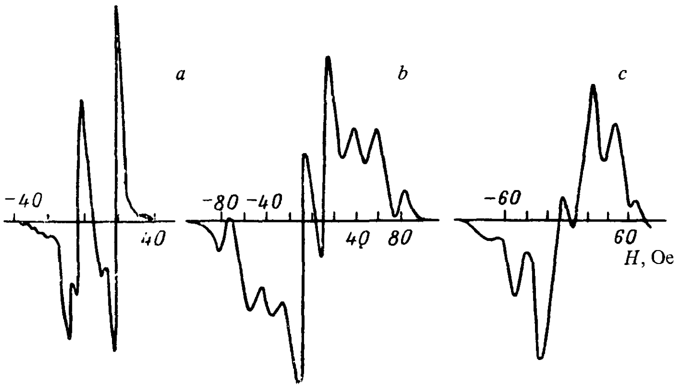


Figure 5. EPR spectra of the free radicals arising as a result of the reaction $H + RH \rightarrow H_2 + R$ at 110–115 K: *a*) malonic acid; *b*) n-hexadecane; *c*) polypropylene.

The principal data for addition reactions (1) are summarised in Tables 2–4. Hydrogen atoms add at 80–140 K to multiple bonds of different types: $C{=}C$, $C{\equiv}C$, $C{=}O$, $C{\equiv}N$, $N{=}O$, $N\begin{smallmatrix}/\!\!/O\\ \diagdown O\end{smallmatrix}$, $N{=}C{=}O$ (Table 2). For olefins and monomers of the vinyl type (methyl methacrylate, vinyl acetate, etc.), the energy of a C–H bond involving a primary carbon atom is greater by several kilocalories than for a bond involving a secondary carbon atom, and hydrogen atoms add mainly to a terminal carbon atom (in conformity with the empirical Markovnikov rule).

Analysis of the molecular olefin hydrogenation products made it possible to determine the relative reactivities of two carbon atoms linked by a double bond. Table 3, which presents data for certain olefins at 90 K, shows that the rate of addition of a hydrogen atom to a primary carbon atom (propene) exceeds by a factor of approximately 100 the rate of addition to a secondary carbon atom. The difference between the rates of addition to primary and tertiary carbon atoms is greater still—it is illustrated by the example of isobutene. Data for the relative reactivities at other temperatures can be found below in Table 8, which also presents values obtained in the study of the effect of atomic deuterium on olefins.

Table 2. The free-radical products of the interaction of atomic hydrogen with unsaturated solid organic compounds [reaction (1)].

Compound	*T*, K	R	References
	$>C{=}C<$		
$CH_2{=}CH_2$	77—90	$CH_3\dot{C}H_2$	7, 26, 35, 36
$CH_2{=}CH{-}CH_3$	77	$CH_3\dot{C}HCH_3$	9, 20, 35
$CH_2{=}C\,(CH_3)_2$	77—90	$CH_3\dot{C}(CH_3)_2$	8, 35, 37
$CH_2{=}CHX$ $(X{=}OCOCH_3, {-}C{\equiv}N$ $C_6H_5,\ COOH,\ CONH_2)$	77	$CH_3\dot{C}HX$	38, 39
$CH_2{=}C\,(CH_3)\,X$ $(X{=}COOCH_3,\ C{\equiv}N$ $COOH,\ CONH_2)$	77	$CH_3\dot{C}(CH_3)X$	38, 39
$CH\,(CH_3){=}CH\,(COOH)$	77	$CH_3CH_2\dot{C}H(COOH)$	39
$C\,(CH_3)\,(COOH){=}CH\,(COOH)$	77—300	$\dot{C}(CH_3)\,(COOH)CH_2(COOH)$	40
$CH_2{=}CH{-}CH{=}CH_2$	77	$CH_2{=}CH{-}\dot{C}H(CH_3)\rightleftarrows$ $\rightleftarrows\dot{C}H_2CH{=}CH(CH_3)$	36
	$-C{\equiv}C-$		
$CH{\equiv}CH$	90	$CH_2{=}\dot{C}H$	7
$CH{\equiv}C\,(COOH)$	77	$CH_2{=}\dot{C}(COOH)$	41
$C(COOX){\equiv}C(COOX)$ $(X{=}H,\ CH_3)$	77	$CH\,(COOX){=}\dot{C}(COOX)$	41
$CH{\equiv}CCH_2X(X{=}Cl,\ Br)$	77	$\dot{C}H{=}CHCH_2X$	41
	$>C{=}O$		
$H_2C = O$	90—120	$H\dot{C}{=}O$	7
$CH_3\overset{/\!/O}{C}{-}H$	77	$CH_3\dot{C}H(OH)$ $CH_3CH_2O^{\cdot}$	38
$CH_3\overset{/\!/O}{C}CH_3$	77	$CH_3\dot{C}(OH)CH_3$ $CH_3\underset{\mid}{C}HCH_3$ $O^{\cdot}$	38
	$-C{\equiv}N$		
$[-CH_2{-}\underset{\mid}{C}H-]_n$ $C{\equiv}N$	140	$[-CH_2{-}\underset{\mid}{C}H-]_n$ $^{\cdot}C{=}NH$	42
	$-N{=}O$		
C_6H_5NO	113	$C_6H_5\dot{N}{-}OH$	43
	$-N\begin{smallmatrix}/\!\!/O\\ \diagdown O\end{smallmatrix}$		
$C_6H_5NO_2$	140	$C_6H_5\underset{\mid}{\dot{N}}O$ OH	44
CH_3NO_2	140	$CH_3\underset{\mid}{\dot{N}}O$ OH	44
$CH_2{=}CHNO_2$	140	$CH_2{=}CH{-}\underset{\mid}{\dot{N}}{=}O$ OH	44
$CH_2{=}C(CH_3)NO_2$	140	$CH_2{=}C\,(CH_3){-}\underset{\mid}{\dot{N}}{=}O$ OH	44
	$-N{=}C{=}O$		
$CH_3N{=}C{=}O$	113	$CH_3NH{-}\dot{C}{=}O$	45
$O{=}C{=}N{-}(CH_2)_6{-}N{=}C{=}O$	123	$O{=}C{=}N{-}(CH_2)_6{-}\dot{N}{-}CH{=}O$	45
$(O{=}C{=}N{-}C_6H_4)_2CH_2$	113	$R{-}\dot{N}{-}CH{=}O$	45

Nitro- and nitroso-groups behave as active acceptors of hydrogen atoms. The addition to a nitro-olefin (nitroethylene, isonitropropene) is selective: virtually only the N=O bonds react. The interaction of the $N{=}C{=}O$ and $N{=}C{=}S$ groups with hydrogen atoms entails the rupture of the $N{=}C$ bond and the site of addition (the nitrogen or carbon atom) depends on the nature of the substituent at these bonds[45].

Hydrogen atoms react very readily with benzene and its derivatives: toluene, biphenyl, phenol, hydroquinone, anisole, etc., with formation of radicals of the cyclohexadienyl type[36,38,46–54]. The EPR spectra of the free radicals arising in these substances are usually poorly resolved and it is not always possible to determine their structure. However, the available data nevertheless permit the conclusion that hydrogen atoms add to the majority of benzene derivatives in the *ortho*- and *para*-positions relative to the substituent (Table 4). 1,3-Disubstituted benzenes react with hydrogen atoms more readily than the 1,2- or 1,4-substituted derivatives[50]. Heterocyclic compounds with aromatic properties, such as furan, thiophen, and their derivatives (Table 4), combine with hydrogen atoms in the 2-position.

Table 3. The relative reactivities of carbon atoms in olefins at 90 K (k_1 and k_1' are the rate constants for the addition of a hydrogen atom to carbon atoms shown to the left and to the right of the double bond respectively)[37].

Olefin	k_1/k_1'
$CH_2=CH-CH_3$	126
$CH_2=C(CH_3)_2$	1000
$CH_3-CH=C(CH_3)_2$	115

Many compounds are involved in hydrogen atom transfer reactions when they interact with atomic hydrogen (Table 5). The free radicals arising in aniline[47], thiophenol[47], allyl alcohol[38], and other compounds as a result of the dissociation of the N-H, S-H, and C-H bonds are to a large extent stabilised owing to conjugation and the reactions therefore proceed at a high rate even at low temperatures. The C-H bonds in other compounds, particularly paraffins, are comparatively strong and the activation energy for a reaction of the type $H + RH \rightarrow H_2 + R$ is 6-9 kcal mole^{-1}.[60] For this reason, it is frequently claimed (see, for example, Refs. 34 and 61) that such reactions cannot be detected at low temperatures (near the boiling point of nitrogen).

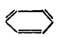
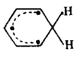
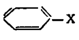
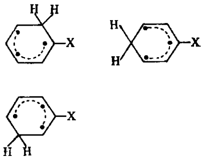
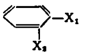
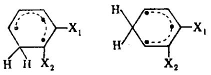
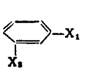
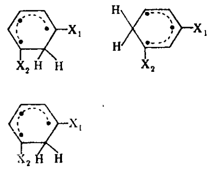
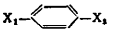
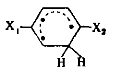
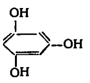
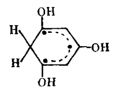
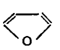
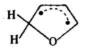
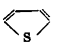
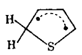
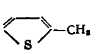
However, studies carried out by the EPR method in recent years revealed the abstraction of hydrogen atoms at a low temperature (in many instances down to 77 K) from a wide variety of compounds, such as cyclohexane, malonic acid, glucose, mannose, and other monosaccharides, tetrahydrofuran, etc. (Table 5). This reaction was observed when many polymers, for example, polyethylene, polypropylene, polyisobutylene, etc. were acted upon by atomic hydrogen[42]. As was to be expected, the site of attack is determined by the weakest C-H bond.

For certain compounds with a complex structure, containing several functional groups, there is a possibility of competition between different modes of reaction. For example, the addition of atomic hydrogen to the aromatic ring and the abstraction of a hydrogen atom from the substituent take place simultaneously in thiophenol, mesitylene, benzyl alcohol, etc.[47,49] When but-2-ene is acted upon by atomic hydrogen, secondary butyl (addition to the double bond) and methylallyl (abstraction of a hydrogen atom from the terminal methyl group) radicals are formed in proportions of 40 : 60.[62] Very many similar examples may be quoted.

Numerous studies have been devoted to the interaction of atomic hydrogen with compounds of biological interest: amino-acids and purine and pyrimidine bases (see the monograph of Pshezhetskii et al.[34] and other reports[32,57,63-73]).

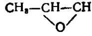
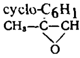
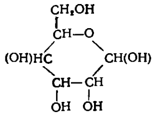
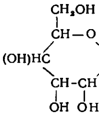
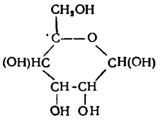
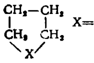
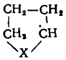
There are numerous data on the modes of reaction of atomic hydrogen with macromolecules. Atomic hydrogen adds to the benzene rings of polymers such as polystyrene, polymethylstyrene, poly(ethylene terephthalate), polyphenylalanine, etc.,[29,31,42,53,54,68] and to the nitrile group of polyacrylonitrile[42]. As already mentioned, atomic hydrogen is abstracted from the main polymer chain in polyethylene, polypropylene, poly(methyl acrylate), poly(methyl methacrylate), polyisobutylene, and certain other polymers[42]. Bombardment of the polymers with hydrogen atoms sometimes leads to the dissociation of C-C bonds with elimination of the side group (poly-L-lysine, poly-L-serine), C-N bonds (poly-L-alanine, poly-L-proline), and C-S bonds (poly-L-methionine)[68,69].

Table 4. The interaction of atomic hydrogen with aromatic compounds [reaction (1)].

	Compound	T, K	R	Refs.
		77—130		36, 38, 46—48
	$X=OH, OCH_3, SO_3H$ $X=CH_3$ $X=CH_2OH, NH_3^+$ $X=Cl$	90 113 90 130		48 49 48 47
	$X_1=OH, X_2=OH$ $X_1=OH, X_2=OCH_3$	90 90		48
	$X_1=X_2=OH$ $X_1=OH, X_2=COOH$ $X_1=COOH, X_2=C(CH_3)_3$	90 298 298		48 48 50
	$X_1=X_2=OH, OCH_3$ $X_1=COOH; X_2=C(CH_3)_3$ $X_1=COOH, X_2=Cl$ $X_1=COOH, X_2=Cl$ $X_1=X_2=COOH$	90 298 187 298 298		48 50 51 50 50
		90		48
		130		47
		130		47
		143		52

Thus at a low temperature atomic hydrogen enters into a wide variety of reactions with the molecules of solid organic substances. It has been established for many compounds that the structures of the free radicals obtained on bombardment with hydrogen atoms and under the influence of high-energy radiation are the same[34,39,41,50,57]. One must therefore suppose that many free radicals, arising in the radiolysis of solid organic substances and responsible for the alteration of their properties, are formed via reactions involving atomic hydrogen.

Table 5. The free-radical products of the interaction of atomic hydrogen with saturated solid organic compounds [the reaction $H + RH \rightarrow H_2 + R$].

Compound	T, K	R	Refs
CH_3OH	90	$\dot{C}H_2OH$	55
CH_3CH_2OH	77—90	$CH_3\dot{C}HOH$	38, 55
$(CH_3)_2CHOH$	77—90	$(CH_3)_2\dot{C}OH$	38, 55
$(CH_3)_2CH(COOH)$	99	$(CH_3)_2\dot{C}(COOH)$	55
$CH_2(COOH)_2$	90—298	$\dot{C}H(COOH)_2$	15, 55, 56
$CH_2(CONH_2)_2$	298	$\dot{C}H(CONH_2)_2$	56
$CH(CH_3)(COX)_2$, X=OH, NH_2	298	$CH_3\dot{C}(COX)_2$	56
$(COOH)CH_2C(CH_3)_2(COOH)$	298	$(COOH)\dot{C}HC(CH_3)_2(COOH)$	40
$(COOH)CH(CH_3)CH(CH_3)(COOH)$	298	$(COOH)\dot{C}(CH_3)CH(CH_3)(COOH)$	40
n-$C_{16}H_{34}$	77—173	n-$C_{16}H_{33}$	15
$NH_3^+CH_2(COOH)$	298	$NH_3^+\dot{C}H(COOH)$	57
$(CH_3)_2CHCH_2CH(NH_2)(COOH)$	298	$(CH_3)_2\dot{C}CH_2CH(NH_2)(COOH)$	57
$(COOH)C_6H_4CH(CH_3)_2$	298	$(COOH)C_6H_4\dot{C}(CH_3)_2$	50
cyclo-C_6H_{12}	133	cyclo-C_6H_{11}	58
	113		58
	110—120	 	59
 X=O, S, SO, SO_2	113—133		58
$C_6H_5CH_2Cl$	130	$C_6H_5\dot{C}HCl$	47
C_6H_5SH	130	$C_6H_5\dot{S}$	47
$C_6H_5NH_2$	130	$C_6H_5\dot{N}H$	47
polymers-$C(CH_3)_2$-CH_2-	77—233	$-C(CH_3)_2-\dot{C}H-$	42, 13, 14
$-CH_2CH_2O-$	99—145	$-CH_2\dot{C}HO-$	42, 13
$-CH_2CH(CH_3)-$	96—173	$-CH_2\dot{C}(CH_3)-$	42, 28
$-CH_2CH(COOCH_3)-$	77—223	$-CH_2\dot{C}(COOCH_3)-$	42, 28
$-C(CH_3)(COOCH_3)CH_2-$	96—203	$-C(CH_3)(COOCH_3)\dot{C}H-$	42, 28

2. Kinetic Constants for Reactions (1) and (2)

The rate constants for all the elementary reactions (1)–(7) have not as yet been determined. The majority of the available kinetic data refer to reactions (1) and (2); the most reliable results have been obtained in studies of the interaction of hydrogen atoms with thin films of olefins[8,9] and with substances adsorbed on the surface of aerosil[13-15,28,29]. The latter method is particularly promising, because it makes it possible to eliminate completely all kinds of diffusion-dependent complications and to measure directly the rate of reaction (1) or (2).

The rate constants for reactions (1) and (2) are calculated from the initial rate of any one of the following processes: absorption of hydrogen, accumulation of free radicals, alteration of the concentration of the initial compound. In all cases it is assumed that $[H]_0 = [H]_{gas}$, i.e. that the concentration of atomic hydrogen in the surface layer of the substance is equal to its concentration in the gas phase—$[H]_{gas}$ is usually determined by EPR.

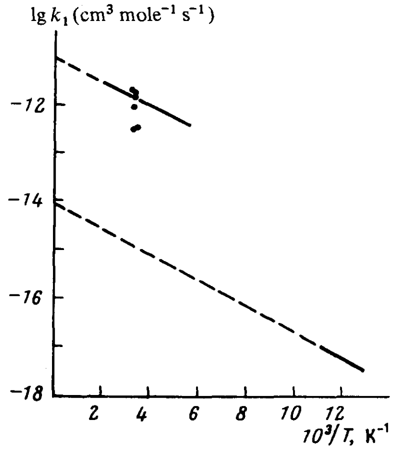


Figure 6. Temperature dependence of the rate constant k_1 for the reaction $H + C_3H_6 \rightarrow C_3H_7$ (for explanation, see text).

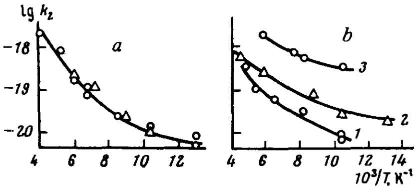


Figure 7. Temperature dependence of the rate constant k_2 for the reaction $H + RH \rightarrow H_2 + R$[14,28]: *a*) polyisobutylene, the triangles denote the values of k_2 for the reaction $D + RH \rightarrow HD + R$; *b*) [1) poly(methyl methacrylate); 2) poly(methyl acrylate); 3) polypropylene]. The constants are referred to a single reacting C–H bond.

Kinetic data for reaction (1) are presented in Table 6 and in Fig. 6 and those for reaction (2) are in Table 7 and in Figs. 7 and 8. For thin films and substances adsorbed in an approximately monomolecular layer on aerosil, the effective activation energy represents the difference between the activation energy for the reaction and the heat of adsorption of atomic hydrogen:

$$E_{\text{eff}} = E - Q_{\text{ads}}. \qquad (31)$$

It has not so far been possible to measure Q_{ads}, but one may suppose that it is small for solid organic substances and that the reactions on the surface proceed with participation of hydrogen atoms arriving directly from the gas phase. In this case $E_{\text{eff}} \simeq E$.

For thick films (acetylene, methylbutene, etc.) and for powders with a small specific surface (thymine, dihydrothymine, etc.), the energy E_{eff} characterises a fairly complex process, including diffusion and dissolution of atomic hydrogen in the given substance. According to the model described by Eqn. (21),

$$E_{eff} = [(E + E_{dif})/2] - Q_{ads}. \qquad (31')$$

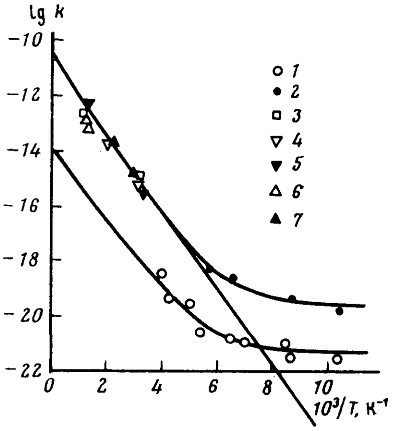


Figure 8. Temperature dependence of the rate constants for different reactions: 1) $H + CH_2(COOH)_2 \rightarrow H_2 + \dot{C}H(COOH)_2$; 2) $H + n\text{-}C_{16}H_{34} \rightarrow H_2 + n\text{-}C_{16}H_{33}$ (Dubinskaya and Yusubov[15]); 3)–7) $H + n\text{-}C_4H_{10} \rightarrow H_2 + n\text{-}C_4H_9$ (Kondrat'ev[60]). The constants refer to a single methylene group.

Table 6 shows that the values of k_1 calculated for propene at 77 K from the rate of change of its concentration agree with one another, but differ from the values determined by another method—from the decrease in the H_2 pressure.

It is noteworthy that in the determination of k_1 from the change in the initial concentration of the reactant, the relative rates of the subsequent reactions (3)–(6) are used. However, analysis has shown that a change by a large factor in the ratio of the rate constants for these reactions has little effect on the calculated k_1. For this reason, the possible inaccuracies in the determination of the role of secondary free-radical reactions can be the cause of the differences between the values of k_1 found by these two methods.

The rate constants for the reaction of atomic hydrogen with solid propene at low temperatures are compared in Fig. 6 with the values measured in the gas phase at elevated temperatures. The upper continuous straight line (177–434 K) was plotted using the results of Kurylo and Preston[75]. The constants at 177–300 K are trustworthy, because they were measured under conditions excluding possible errors associated with side reactions (the abstraction of hydrogen atoms from propene, the decomposition of excited propyl radicals, etc.). The data of other workers at room temperature (circles), summarised by Jones et al.[5] and Kondrat'ev[60], are also presented. The lower straight line refers to the reaction of atomic hydrogen with solid propene and was plotted using the following values: $E_1 = 1.5$ kcal mole^{-1} and $k_1(77\ K) = 3 \times 10^{-18}$ cm^3 s^{-1}, which we believe to be the most trustworthy. Fig. 6 shows that the activation energies in the gas and solid phases are similar, but the pre-exponential factor in the Arrhenius equation for the reaction with solid propene is appreciably lower (by three orders of magnitude).

The values of k_1 for polystyrene at a low temperature, determined by two different methods (from the initial rate of formation of free radicals and from the decrease of the

Table 6. Critical constants for the addition of atomic hydrogen to certain unsaturated compounds.

Compound	Characteristics of specimen	Measured parameter	T, K	k_1, cm^3 s^{-1}	Temp. range**	E_{eff}, kcal mole^{-1}	Refs.
Propene	film, $l = 10^{-5}$ cm	$-dH_2/d\tau$	77	$\sim 8 \cdot 10^{-17}$*	—	—	9
	film, $l = 10^{-4}$ cm	$-d[M]/d\tau$	77	$\sim 4 \cdot 10^{-18}$*	77—100	1.5	20
	film, $l = 6 \times 10^{-4}$ cm	$-d[M]/d\tau$	77	$3 \cdot 10^{-18}$	—	—	17
	film, $l = 10^{-4}$-10^{-3} cm	$-dH_2/d\tau$	—	—	63—78	<0,5	74
Isobutene	film, $l = 10^{-4}$-10^{-3} cm	$-dH_2/d\tau$	77		63—78	<0.7	74
	film, $l \approx 10^{-5}$ cm	$-dH_2/d\tau$	77	$5 \cdot 10^{-18}$	—	—	8
3-Methylbut-1-ene	film, $l = 10^{-4}$-10^{-3} cm	$-dH_2/d\tau$	—	—	63—78	3.0	74
2-Methylbut-1-ene	film, $l = 10^{-4}$-10^{-3} cm	$-dH_2/d\tau$	—	—	63—78	2.8	74
Acetylene	film, $l = 10^{-4}$-10^{-3} cm	$-dH_2/d\tau$	—	—	63—78	1.0	74
Toluene	film, $l = 10^{-4}$-10^{-3} cm	$-dH_2/d\tau$	—	—	78—160	0.7	74
Phenylacetylene	film, $l = 10^{-4}$-10^{-3} cm	$-dH_2/d\tau$	—	—	78—150	0,5	74
Thymine	powder, particle size 60–100 μm	$d[R]/d\tau$	—	—	120—330	1,2	72
Uracil	aerogel ("fluff")	$d[R]/d\tau$	—	—	190—300	2	73
	powder, particle size 60–100 μm	$d[R]/d\tau$	—	—	190—300	1,5	73
Polystyrene	aerogel, $s_{sp} = 20$ m^2 g^{-1}	$d[R]/d\tau$	295	$7 \cdot 10^{-18}$	—	—	53
	polymer adsorbed on aerosil in a monomolecular layer, $s_{sp} = 200$ m^2 g^{-1}	$d[R]/d\tau$ $d[R]/d\tau$ $-dH_2/d\tau$	77 123 123	$5 \cdot 10^{-20}$ $11.5 \cdot 10^{-19}$ $9.8 \cdot 10^{-19}$	77—163	1.3	29

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*The concentration of hydrogen atoms was calculated and not measured (see text).

**Temperature range in which the activation energy E_{eff} was measured.

pressure of molecular hydrogen) agree satisfactorily (Table 6). The dependence of the rate constant for the addition of atomic hydrogen to polystyrene on temperature in the range 77–163 K may be represented by the expressions $k_1 = 10^{-15.8\pm0.4} \exp[(-1300 \pm 200)/RT]$ cm^3 s^{-1}.[29] These data refer to polystyrene adsorbed in an approximately monomolecular layer on the surface of aerosil ($s_{sp} \simeq 200$ m^2 g^{-1}) and the measured kinetic constants presumably characterise the rate of the chemical reaction itself.

Table 7. Kinetic constants for the reaction $H + RH \rightarrow H_2 + R$ (the constants k_2 were determined throughout for one reacting C–H bond).

Reacting compound	T, K	E_{eff}, kcal mole^{-1}	k_2, cm^3 s^{-1}	Refs.
Deuteropolyethylene*	170—430	2—3	—	76
Dihydrothymine**	140—330	2.5	—	72
Dihydrouracil***	190—300	2	—	73
Malonic acid	96	0.6	$1.8\cdot10^{-22}$	15
	253	6.0	$1.3\cdot10^{-19}$	
n-Hexadecane	77	0.4	$1.5\cdot10^{-21}$	15
	173	3.2	$2.2\cdot10^{-19}$	
Poly(methyl acrylate)	77	0.3	$1.8\cdot10^{-20}$	28
	223	2.0	$5.2\cdot10^{-19}$	
Poly(ethylene oxide)	99		$1.6\cdot10^{-20}$	13
Poly(methyl methacrylate)	96	0.4	$7.5\cdot10^{-21}$	28
	203	2.2	$3.2\cdot10^{-19}$	
Polypropylene	96	0.3	$3.2\cdot10^{-19}$	28
	173	1.3	$1.6\cdot10^{-18}$	
Polyisobutylene	77	0.4	$5.5\cdot10^{-21}$	14
	233	4.0	$2\cdot10^{-18}$	

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*Specimen in the form of a powder.

**Powder with a particle size of 60–100 μm.

***Aerogels; in the remaining cases the substance was adsorbed on aerosil.

It is of interest to compare the constants k_1 for different compounds at a single temperature; unfortunately only a limited number of such data are available. Table 6 shows that the rate constants for the addition of atomic hydrogen to propene and isobutene (77 K) are approximately the same and exceed the corresponding constant for the addition to the benzene rings of polystyrene by two orders of magnitude. The ratio of the rates of addition of atomic hydrogen at 90 K to the $CH_2 = CH-$ (propene and but-1-ene) and $-CH=CH-$ (*trans*-but-2-ene) bonds is ten[37]. An approximately the same ratio of the rates is observed for the addition of atomic hydrogen to the terminal and inner double bonds in hexa-1,4-diene[37].

Interesting results were obtained in a kinetic study of reaction (2): $H + RH \rightarrow H_2 + R$ (Table 7 and Figs. 7 and 8). The rate of reaction and the concentration of hydrogen atoms (in the gas phase) were in all cases measured by EPR. The majority of kinetic data refer to substances adsorbed in a thin layer (not more than 5–10 μmole m^{-2}) on aerosil with a specific surface of 200 m^2 g^{-1}.

The principal characteristic feature of the low-temperature reaction $H + RH \rightarrow H_2 + R$ is the absence of a linear dependence of $\lg k_2$ on $1/T$. The plot of $\lg k_2$ against $1/T$ is a concave curve[14,15,28], i.e. the rate constant diminishes much more slowly than would follow from the Arrhenius law as the temperature is reduced. The concave shape of the curves is pronounced in those cases where it was possible to investigate the reaction over a comparatively wide range of temperatures, for example, for polyisobutylene (Fig. 7*a*) and malonic acid (Fig. 8, curve *1*).

The rate constants for reactions at a low temperature are high [thus the values of k_2 at 77 K for n-hexadecane, poly(methyl methacrylate) and polyisobutylene are in the range 10^{-21}–10^{-20} cm^3 s^{-1}] and exceed by many orders of magnitude the values which would be expected if the Arrhenius law held. Fig. 8 compares the rate constants for the reactions of atomic hydrogen with the methylene groups of n-hexadecane (solid phase, 77–188 K) and n-butane (gas phase, 300–500 K).

The plot shows that the rate constant for the reaction at 77 K exceeds the extrapolated value by ten orders of magnitude. At 77–120 K the reaction rate is almost independent of temperature. The effective activation energy in this temperature range is < 1 kcal mole^{-1}.

3. Isotope Effects in Reactions (1) and (2)

As mentioned at the beginning of Section III, the ratio of the rate constants for the addition of atomic hydrogen in the two possible positions relative to the $\rangle C=C \langle$ double bond [reactions (1) and (1′)] depends on the nature of the substituents at the carbon atoms (Table 3). The ratio increases when the olefin is acted upon by atomic deuterium; under these conditions, the greater the ratio k_1/k_1', the greater the isotope effect (Table 8)[37]. It has been established[37] that, when atomic hydrogen reacts with propene and deuteropropene, the relative rates of reactions (1) and (1′) are the same, i.e. there is no isotope effect.

Table 8. The isotope effects in reactions involving the addition of hydrogen and deuterium atoms to olefins[37] (k_1 and k_1' are the rate constants for the addition of hydrogen or deuterium atoms to carbon atoms shown to the left and to the right of the double bond respectively).

Olefin	T, K	$(k_1/k_1')_H$	$(k_1/k_1')_D$	$\frac{(k_1/k_1')_D}{(k_1/k_1')_H}$
$CH_2=CH-CH_3$ or $CD_2=CD-CD_3$	90	126	398	3.1
	77	167	575	3.4
$CH_3-CH=CH-CH_2-CH_3$ (cis)	90	1.48	1.46	1.0
$CH_3-CH=C(CH_3)_2$	77	115	234	2.0
	90	115	233	2.0
	113	102	155	1.5
	143	53	75	1.4

The rate of the reaction $H + RH \rightarrow H_2 + R$ hardly changes when hydrogen atoms are replaced by deuterium[77]. The rate constants for the reactions in these two instances are plotted in Fig. 7*a*. Evidently all the points lie on a single curve. On the other hand, the rate of the hydrogen atom transfer reaction is very sensitive to isotope substitution in the structure of the reacting molecule[28,77]. Fig. 9 presents data for the kinetic isotope effects in the reactions of atomic hydrogen with poly(methyl methacrylate) and deuteropoly(methyl methacrylate) (all the hydrogen atoms have been replaced by deuterium atoms and the deuterium content in the isotope-substituted position is 98.9%). The measured isotope effects (curve *1*) are compared with the values calculated from the equation $k_H/k_D \simeq \exp(0.15\, h\nu_{C\text{-}H}/kT)$ (Here $\nu_{C\text{-}H} = 9 \times 10^{13}$ s^{-1} is the stretching vibration frequency of the C–H bonds, h the Planck constant, and k the Boltzmann constant)[78]. Fig. 9 shows that the experimental values exceed the calculated data over the entire temperature range (165–300 K), the discrepancy increasing at low temperatures. The calculated isotope effect at 165 K is 45, while the experimental value is $\geqslant 260$.

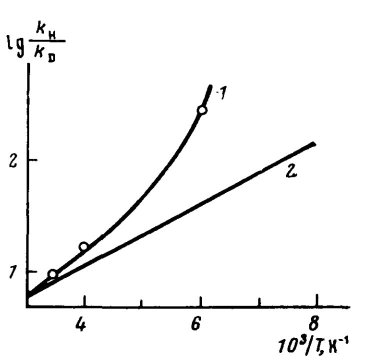

Figure 9. Temperature dependence of the isotope effect k_H/k_D for the reactions of hydrogen atoms with poly(methyl methacrylate) and deuteropoly(methyl methacrylate)[28]: 1) experimental values; 2) linear plot based on calculated values (see text).

Thus kinetic isotope effects of two types were observed—those associated with the replacement of (1) atomic hydrogen by atomic deuterium and (2) of H atoms by D atoms in the structure of the reacting molecule. Isotope effects of the first type are characteristic of addition reactions where the second effect is absent, while the situation is reversed in hydrogen atom transfer reactions.

IV. QUANTUM-MECHANICAL EFFECTS IN LOW-TEMPERATURE REACTIONS

The possible role of the tunnel effect in chemical kinetics has been frequently discussed theoretically[79-82]. It has been shown experimentally that tunnelling must be taken into account in a whole series of reactions involving electron transfer (oxidation-reduction reactions and radiation-chemical and photochemical processes). The mass of the hydrogen atom exceeds that of the electron by a factor of 1841, which reduces sharply the probability of the passage of H through the barrier. For this reason, the tunnel effect in reactions involving the transfer of a proton or a hydrogen atom can be manifested distinctly only at low temperatures. A number of kinetic consequences arise from the possible tunnel migration of a hydrogen atom through the barrier: deviations from the Arrhenius law, extremely large isotope effects when the H atom in the structure of the reacting molecule is replaced by a D or T atom (k_H/k_D or k_H/k_T), a nonlinear relation between $\lg(k_H/k_D)$ and $1/T$, etc. These facts were established in a study of the interaction of hydrogen atoms with solid organic substances at low temperatures, namely $H + RH \rightarrow H_2 + R$. The tunnel mechanism of this reaction is confirmed by calculations of the dependence of the reaction rate constant on temperature, taking into account the passage through the barrier.

The reaction rate constant can be represented in the usual Arrhenius form:

$$k = A\gamma \exp(-V/RT), \tag{32}$$

where V is the height of the potential barrier in the reaction, A the pre-exponential factor, and $\gamma = w_{qu}/w_{cl}$ the correction for tunnelling or the "tunnel" correction (w_{qu} and w_{cl} are the "quantum" and "classical" reaction rates).

An exact calculation of the "tunnel" correction is impossible without knowing the potential surface for the reaction. Simplified models are used in approximate calculations. It is assumed to a rough approximation[79,82] that the activation barrier is one-dimensional and that the system is in thermal equilibrium. For such a system, we have:

$$\gamma = \exp\frac{V}{kT}\int_0^\infty \frac{1}{kT}\, G(W)\exp\left(-\frac{W}{kT}\right)\mathrm{d}W, \tag{33}$$

where W is the energy of the reacting species, $G(W)$ the probability of the tunnel reaction or the permeability of the barrier, which depends only on its width and height when its shape is specified, and k is the Boltzmann constant.

The experimental data for the reaction $H + RH \rightarrow H_2 + R$ at low temperatures agree satisfactorily with the results of the calculation carried out in accordance with this model[13,15,83]. In the calculations the barrier was assumed to have the parabolic shape; Bell[80] obtained an exact solution of the integral Eqn. (33) for such a barrier:

$$\gamma = \frac{e^{\alpha}}{\beta-\alpha}\left(\beta e^{-\alpha} - \alpha e^{-\beta}\right). \tag{34}$$

Here

$$\alpha = V/kT,\ \beta = \frac{2\pi^2}{h} d \cdot (2mV)^{1/2},$$

where d is the effective half-width of the barrier, m the reduced mass of the tunnelling species, and h the Planck constant.

The rate constants calculated for the reactions involving malonic acid and n-hexadecane (continuous curves) are compared in Fig. 8 with the measured values (designated by circles). The parameters of the barrier and the pre-exponential factors used in the calculation are listed in Table 9. It is striking that the rate constants for the reactions involving n-butane and n-hexadecane (per methylene group) fit on a single smooth $\lg k - 1/T$ curve, which satisfies the parameters listed in Table 9 for the reaction

$$H + C_nH_{2n+2} \rightarrow H_2 + C_nH_{2n+1}.$$

Thus the temperature dependence of the rate of this reaction may be accounted for over a very wide range (100–1000 K) on the assumption that the potential surface for the reaction remains unchanged on passing from the gas phase (330–1000 K) to the solid phase (100–173 K) and that the deviation from the Arrhenius law is due to the tunnel mechanism of the reaction at a low temperature.

Table 9 also presents the parameters of the activation barrier for a number of other reactions for which the appropriate calculations have been made[83]. In all cases the calculated and experimental results agreed satisfactorily. The effective half-widths of the barriers in these reactions are in the range 0.5–0.65 Å (Table 9) and are comparable with the values calculated by Caldin[82] for proton transfer in the liquid phase.

Table 9. Certain parameters adopted in the calculation of the "tunnel" correction (parabolic barrier)[83].

Reaction	T, K	V, kcal mole^{-1}	d, Å	A, cm^3 s^{-1}
$\dot{H} + -(CH_3)_2C-CH_2-C(CH_3)_2- \rightarrow H_2 + -(CH_3)_2C-\dot{C}H-C(CH_3)_2-$	100—180	6.0	0.65	$5\cdot10^{-11}$
$\dot{H} + -CH_2CH_2O- \rightarrow H_2 + -CH_2\dot{C}HO-$	100—150	6.7	0,57	$5\cdot10^{-11}$
$\dot{H} + C_nH_{2n+2} \rightarrow H_2 + C_nH_{2n+1}$	100—1000	7.0	0.58	$3\cdot10^{-11}$
$\dot{H} + CH_2(COOH)_2 \rightarrow H_2 + \dot{C}H(COOH)_2$	100—250	6.1	0.51	10^{-14}

Thus calculations carried out in terms of a rough approximation showed that the rate constants for the reaction $H + RH \rightarrow H_2 + R$ and the form of the temperature dependence of lg k_2 can be satisfactorily explained on the assumption of tunnelling.

Calculations of the ratios k_1/k_1' for the addition of atomic hydrogen to olefins have been carried out taking into account tunnelling (Table 8).[37] It was assumed in these calculations that the addition to two carbon atoms can be described by two one-dimensional barriers, taking into account the asymmetry of the barriers. The parameters of each barrier were varied as follows: the height from 1.2 to 4.5 kcal mole^{-1} and the effective half-width from 0.25 to 0.75 Å. The authors[37] were unable to achieve the agreement of all the experimental k_1/k_1' ratios at different temperatures with the calculated values whatever the combination of the quantities characterising the height and width of the barrier (the calculations were performed for rectangular and Eckart forms of the barrier). Nevertheless one may agree with the authors' conclusions that tunnelling is the only mechanism which permits an explanation of the isotope effects observed in the addition reaction. The discrepancies between the experimental and calculated values are probably associated with the fact that the one-dimensional barrier model is relatively unsuitable for the description of the reaction in the present instance.

V. REACTIONS OF FREE RADICALS WITH HYDROGEN ATOMS AND WITH ONE ANOTHER AT A LOW TEMPERATURE

Hydrogen atoms react with free radicals at a low temperature via recombination [reaction (3)] and disproportionation [reaction (4)] mechanisms. The elementary constants k_3 and k_4 for low-molecular-weight free radicals have not been measured, but attempts have been made[22,24] to estimate the ratios of these constants for certain systems. The few available data for reactions of the type R + H are summarised in Table 10, which shows that the disproportionation reaction predominates for alkyl radicals at a low temperature. This conclusion applies also to isotope-substituted radicals, without hydrogen atoms, such as C_3D_6T.

The overall rate constants for the reaction with atomic hydrogen ($k_3 + k_4$) were measured in the range 77–220 K for polymeric free radicals of different structures[28]. To a first approximation, the temperature dependence of $k_3 + k_4$ obeys the Arrhenius law. The activation energies for the reactions are in the range 0.4–0.9 kcal mole^{-1} and the pre-exponential factors are in the range $10^{-14.3}$–$10^{-15.6}$ cm^3 s^{-1} (Table 11), i.e. are smaller by 2–4 orders of magnitude than the collision numbers Z for the systems investigated ($Z \simeq 10^{-11}$ cm^3 s^{-1}).

Table 10. The ratios of the rate constants for the disproportionation and recombination reactions.

Reactions	T, K	k_4/k_3	References
$H + s\text{-}C_4H_9$	90	1.9	22
$T + iso\text{-}C_3H_6T$	63	3,55	24
$T + C_3D_6T$	63	3,05	24

Table 11. Parameters of the Arrhenius equation for the reaction between R(ROO) and atomic hydrogen[28,29].

Polymeric free radicals	Temp. range, K	E, kcal mole^{-1}	$-\lg A$ (cm^3 s^{-1})
$-C(CH_3)_2-\dot{C}H-C(CH_3)_2-$	77—163	0.4	~15.6
$-C(CH_3)(COOCH_3)-\dot{C}H-C(CH_3)(COOCH_3)-$	96—203	0.9±0.3	14.7±0.3
$-CH_2-\dot{C}(COOH_3)-CH_2-$	77—223	0,5±0.2	15.5±0.3
$-CH_2-\dot{C}(CH_3)-CH_2-$	96—173	0.5±0.3	14.4±0.5
$-CH_2-C(C_6H_5)-CH_2-$	77—163	0,8±0,1	14.3±0.3
ROO· poly(vinyl acetate)	113—173	1.2±0,1	14,8±0.1

These values were obtained from the analysis of kinetic curves for the accumulation of free radicals, which does not allow the separate determination of k_3 and k_4. In order to discover which reaction predominates—recombination or disproportionation—additional measurements are necessary using other methods (analysis of molecular products, the study of the deuterium-hydrogen exchange, monitoring of the pressure variation, etc.). It has been possible to establish for polystyrene[29] that free radicals (of the cyclohexadienyl type) interact with hydrogen atoms (at 123–163 K) via a recombination mechanism, which leads to partial hydrogenation of the aromatic rings. Presumably this reaction is the cause of the appearance of cyclohexadiene rings, which were detected by infrared spectroscopy in polystyrene irradiated by fast electrons[84].

The free radicals arising as a result of reactions (1) and (2) can react not only with hydrogen atoms but also with one another. The rate of reaction of the radicals in the solid phase is usually limited by their mobility. The kinetics and mechanism of the destruction of free radicals in the solid phase constitute an independent problem and numerous studies have been devoted to it. We shall consider only the question of the relative rates of the reactions leading to the destruction of free radicals when they interact with one another: the recombination [reaction (5)] and disproportionation [reaction (6)] reactions. The ratios k_{disp}/k_{rec} (k_6/k_5) for the free radicals formed when solid organic compounds are acted upon by hydrogen or tritium atoms are listed in Table 12, which also includes the values for the free radicals obtained by other methods. Analysis of these data reveals the following fundamental features.

(1) The ratio k_{disp}/k_{rec} depends on the structure of the radicals. For primary alkyl radicals (methyl–ethyl, ethyl–ethyl), the ratio is small and amounts to 0.2–0.3 at 80–90 K, i.e. the recombination reaction predominates. For secondary radicals (isopropyl, s-butyl, s-pentyl, cyclohexyl), the ratio k_{disp}/k_{rec} increases and is in the range 2–11 according to different data. The difference between the relative rates of disproportionation and recombination is even greater for tertiary butyl and pentyl radicals. The disproportionation reaction is virtually the only pathway to the destruction of these radicals at a low temperature.

Table 12. The ratios of the rate constants for the disproportionation and recombination reactions in the solid-phase interaction of certain free radicals with one another.

Free radicals[a]	T, K	k_{disp}/k_{rec}	Matrix	References
$\dot{C}H_3+\dot{C}_2H_5^*$	82	0,174	$CH_3N_2C_2H_5$	85
	82	0.183	iso-octane	
	82	0,196	glycol	
$2\dot{C}_2H_5^*$	89	0.198	azoethane	86, 87
	89	0.309	toluene	
	89	0.325	propanol	
	79	0.304	toluene	
	78	0,187	azoethane	
	78	0.327	glycol	
$\dot{C}_2H_5+\dot{C}_2H_4T$	63	0.83	ethylene	26
$2\dot{C}_2H_4T$	63	0.77	ethylene	
$2\dot{C}_2D_4T$	63	0,75	ethylene	
2iso-$\dot{C}_3H_7$	90	6	propane	37
	77	8—10	propane, butane	9, 20, 21, 37
	77	3	propene	17
	77	2*	azoisopropane	22
	63	22	propane	37
2iso-$\dot{C}_3H_6T$	77	5.5	propene	23
	63	5.9	propene	
2s-$\dot{C}_4H_9$	90	11	propane	22
2t-$\dot{C}_4H_9$	90	500	propane	37
2s-$\dot{C}_5H_{11}$	90	6,4	propane	88
$2CH_3\dot{C}HCH_2CH{=}CH_2$	90	7.6	propane	88
2t-$\dot{C}_5H_{11}$	90	1566	propane	89
t-$\dot{C}_5H_{11}$ + s-$\dot{C}_4H_9$	90	35	propane	89
2cyclo-$\dot{C}_6H_{11}$	160—190	5	cyclohexane	90
	112	2.7	cyclohexene	91
	77	49	cyclohexene	91
	77	1	cyclohexane	35
$2CH_3{-}\dot{C}H{-}CH{=}CH_2$	90	<0.01	propane	88
$2CH_3{-}\dot{C}H{-}CH{=}CH(CH_3)$	90	<0.01	propane	88
$2CH_3{-}\dot{C}(CH_3){-}CH{=}C(CH_3)_2$	90	<0.01	propane	88

[a] The free radicals were generated by exposing the corresponding olefin or diene to hydrogen or tritium atoms; in the instances denoted by asterisks the free radicals were obtained by the photodecomposition of azo-compounds.

In contrast to alkyl radicals, allyl radicals are destroyed exclusively via a recombination mechanism (Table 12).

(2) The ratio k_{disp}/k_{rec} is sensitive to the nature of the matrix in which the free radicals are present. The physical state of the substance in which the radicals are distributed plays an important role under these conditions. Thus the ratios and the rates of recombination and disproportionation are different in vitreous and crystalline matrices[92].

(3) The ratio k_{disp}/k_{rec} increases as the temperature is reduced, which indicates a higher activation energy for the recombination reaction than for the disproportionation reaction. It follows from the data in Table 12 that the difference $E_{rec} - E_{disp}$ usually amounts to several hundreds of cal mole^{-1}.

Similar features, albeit not quite so pronounced, are also observed for the reactions of free radicals with one another in the liquid phase[93,94]. The ratio k_{disp}/k_{rec} also depends in this case on the structure of the reacting radicals and on the type of solvent, increasing as the temperature is reduced.

Thus fairly extensive experimental data concerning the nature of the interaction of free radicals with one another in the solid phase, analysis of which is useful in the study of the mechanisms of solid-phase reactions and for the elucidation of the structure of the transition complex in recombination and disproportionation reactions, have now accumulated. It has been suggested at one time that these two reactions have a common transition complex, which aroused controversy and stimulated a number of investigations[94]. The dependence of k_{disp}/k_{rec} on the nature of the matrix and temperature (Table 12) shows that the hypothesis of two types of transition complex is more correct. This problem is discussed in greater detail in a special review[94].

VI. DIFFUSION AND RECOMBINATION OF HYDROGEN ATOMS IN SURFACE LAYERS

Data on the diffusion, solubility, adsorption, and recombination of hydrogen atoms in solid organic substances are important for understanding the mechanism of the interaction of gaseous atomic hydrogen with such substances. Unfortunately there is almost no information of this kind, mainly owing to the lack of direct methods of measurement. For this reason, this last section represents merely an attempt at a compilation in one place of the scattered values which are sometimes rough estimates based on indirect data.

Table 13. The diffusion coefficients D and rate constants for the recombination of hydrogen atoms (k_7) in frozen hydrocarbons at 77 K.

Hydrocarbon	D, cm^2 s^{-1}	k_7, cm^3 s^{-1}
Propene	$3\cdot10^{-7}$ (27)	$2\cdot10^{-14}$
Propane	$2\cdot10^{-4}$	$\sim10^{-11}$
n-Butane	$5\cdot10^{-4}$ (9)	$3\cdot10^{-11}$
Isobutene	$2\cdot10^{-8}$ (8)	$1\cdot10^{-10}$ ($2\cdot10^{-12}$ (8))

Note. Figures in round brackets denote references (Ed. of translation).

The diffusion coefficients of hydrogen atoms in certain frozen hydrocarbons are listed in Table 13. The estimates of D are based on the H-diffusion model where no account was taken of the mobilities of other reacting species (see Section II), so that the tabulated values do not correspond entirely to real systems.

The recombination rate constants k_7 for hydrogen atoms in a layer of frozen hydrocarbon (Table 13) were calculated on the hypothesis that each collision leads to interaction and that the rate of reaction (7) is limited by the diffusion of hydrogen atoms. Then

$$k_7(\mathrm{cm^3\,s^{-1}}) = 4\pi\rho D\,, \tag{35}$$

where ρ is the collision radius of the hydrogen atom, assumed to be 0.5 Å in the calculations.

Table 13 also lists the value $k_7 = 2 \times 10^{-12}$ proposed for isobutene[8].

The values of D and k_7 for propane were estimated from calorimetric measurements[3,27]. The heat evolved in a layer of propane amounts to 6% of that evolved in a layer of propene with the same thickness. Assuming that the evolution of heat is caused in the first case by hydrogenation and in the second by reaction (7) (as will be shown below, this is apparently true), one can write

$$w_7/w_{\mathrm{hydr}} = 0.06\ Q_{\mathrm{hydr}}/Q_7 = 0{,}08$$

where w_7 and Q_7 are the rate and heat of recombination of hydrogen atoms in propane and w_{hydr} and Q_{hydr} are the rate and heat of hydrogenation of propene. Under the experimental conditions, we have

$$w_{\mathrm{hydr}} \simeq 2k_1[\mathrm{H}][\mathrm{C_3H_8}],\ w_7 = k_7[\mathrm{H}]^2.$$

Hence

$$k_7 \sim \frac{2k_1[\mathrm{C_3H_8}]}{[\mathrm{H}]} \cdot \frac{w_7}{w_{\mathrm{hydr}}} \simeq \frac{2k_1[\mathrm{C_3H_8}]}{[\mathrm{H}]} \cdot 0{.}08 \simeq \frac{0{,}16k_1[\mathrm{C_3H_8}]}{[\mathrm{H}]}\,.$$

When $[\mathrm{H}] = 10^{14}$ cm^{-3}, we have $k_7 \simeq 10^{-11}$ cm^3 s^{-1}.

D for propane, calculated by Eqn. (35), is 2×10^{-4} cm^2 s^{-1} and is close to the diffusion coefficient in n-butane.

We shall now trace the fate of hydrogen atoms in a solid reacting substance. The destruction of hydrogen atoms is possible in the course of reactions (1)–(4) and (7). We shall denote by w_{add} the rate of destruction of hydrogen atoms as a result of the chemical reaction with an unsaturated compound M and by w_{abs} the rate of destruction due to the reaction with a saturated compound RH. At a steady-state concentration of free radicals, we have

$$w_{\mathrm{add}} \simeq 2k_1[\mathrm{H}][\mathrm{M}],\ w_{\mathrm{abs}} \simeq 2k_2[\mathrm{H}][\mathrm{RH}].$$

Then

$$w_7/w_{\mathrm{add}} = \frac{k_7[\mathrm{H}]}{2k_1[\mathrm{M}]}\ \text{and}\ w_7/w_{\mathrm{abs}} = \frac{k_7[\mathrm{H}]}{2k_2[\mathrm{RH}]}\,.$$

Thus the ratio of the rates of the corresponding processes is determined by the constants k_7 and k_1 (k_2) and the concentration of atomic hydrogen in the layer of the reacting substance. For frozen olefins (propene, isobutene), k_7(77 K) = 10^{-12} cm^3 s^{-1}, which is probably close to the real value. The constant $k_1 \simeq 10^{-18}$ cm^3 s^{-1} (Table 6). Hence $w_7/w_{\mathrm{add}} \simeq 10^{-16}[\mathrm{H}]$. Since $[\mathrm{H}] \leqslant 10^{14}$ cm^{-3} under the experimental conditions, it follows that $w_7 \simeq 10^{-2} w_{\mathrm{add}}$, i.e. hydrogen atoms are destroyed preferentially as a result of the hydrogenation of the olefin.

For the hydrogen atom transfer reaction $\mathrm{H + RH \rightarrow H_2 + R}$ (polyisobutylene), k_2(77 K) = 5×10^{-21} cm^3 s^{-1}. If the value of k_7 is the same as in the previous example, then $w_7/w_{\mathrm{abs}} = 10^{-14}[\mathrm{H}]$. Hence we obtain $w_7 \simeq w_{\mathrm{abs}}$ for $[\mathrm{H}] = 10^{14}$ cm^{-3} and $w_7 < w_{\mathrm{abs}}$ for $[\mathrm{H}] < 10^{14}$ cm^{-3}. Thus under the real experimental conditions the rate of recombination of hydrogen atoms in polyisobutylene at 77 K is comparable to the rate of their destruction via chemical interaction with the polymer. At low concentrations of atomic hydrogen, the destruction of radical species in reactions (2)–(4) predominates.

The heterogeneous recombination of hydrogen atoms on the surfaces of certain organoelemental polymers has been studied in a number of investigations[5,95,101,102]. The rate of destruction of atoms on any surface is characterised by the probability of recombination ϵ, which is defined as the ratio of the rate of heterogeneous recombination to the frequency of the impacts by atoms on the surface. It is usually believed[5] that the rate of recombination of hydrogen atoms on the surfaces of polymeric films obeys (as for Pyrex) first-order kinetics, but this conclusion requires further confirmation and ϵ may depend on the concentration of atomic hydrogen in the gas phase. The probabilities of the recombination of atomic hydrogen on the surfaces of certain polymers at room temperature are listed below:

Polymer	ε	Literature
Polytetrafluoroethylene	10^{-4}	95
	$\sim 10^{-6}$	101
Polychlorotrifluoroethylene	$4 \cdot 10^{-4}$	95
Chloromethylsilane polycondensation products (Drifilm)	$4 \cdot 10^{-4}$	95
	$2 \cdot 10^{-5}$	102

The rate of hydrogenation of propene hardly changes when it is coated by a thin film of propane[1,3,27], which indicates a low rate of recombination of hydrogen atoms in the propane layer. According to Ponomarev's estimate[27], the probability of the recombination of atomic hydrogen on the surface of propane (at 77 K) is 6×10^{-5}.

There are no other more detailed literature data for the rates and mechanisms of the recombination of hydrogen atoms on the surfaces of solid organic substances. We believe that research on the heterogeneous recombination of atomic hydrogen at low temperatures, where its rate still depends on the heat of the physical adsorption of hydrogen atoms on the surface of the substance, is urgently required. One may hope that such research will make it possible to estimate the heats of adsorption of various compounds and to approach more closely the mechanisms of the chemical reactions of atomic hydrogen with solid organic substances.

VII. CONCLUSION

The interaction of thermal hydrogen atoms with a wide range of solid organic substances has been investigated. The mechanisms of the reactions leading to the formation of free radicals have been unambiguously established for the vast majority of the compounds. The mode of these reactions is determined by the chemical structure of the reactant and is as a rule the same in the gas and liquid phases. However, in those cases where there is a possibility of two or more reaction pathways, the low-temperature reaction in the solid phase proceeds via the pathway which requires the lowest activation energy. For example, the main pathway in the reaction of atomic hydrogen with toluene at 113 K involves addition to the aromatic ring[49]: $\mathrm{H + C_6H_5CH_3 \rightarrow C_6H_6CH_3}$, whereas in the gas phase at high temperatures hydrogen atoms are abstracted from the methyl group[96] and the reaction $\mathrm{H + C_6H_5CH_3 \rightarrow C_6H_6 + CH_3}$ takes place[97].

The ratio of the rate constants for the addition of hydrogen atoms in two different positions relative to the double bond of the olefin increases as the temperature is reduced. Thus the ratio for propene increases from 21 (300 K, gas phase) to 189 (63 K, solid phase)[37]. These two examples therefore show that the reactions are more selective at a low temperature.

The specific features of the solid phase and low temperatures affect the kinetics of the individual stages of the interaction of atomic hydrogen with solids; they are manifested in two ways. On the one hand, the mechanism of the chemical reactions is simplified, since many secondary free-radical processes occurring in the gas phase do not take place in the solid phase at fairly low temperatures owing to the limited mobility of the molecules and free radicals. Furthermore, vibrationally excited species are formed in the gas phase, while the solid phase promotes their effective deactivation. For this reason, reactions involving the decomposition of excited species as well as possible reactions of hot radicals[5,61,98,99] are ruled out when the kinetics of solid-phase processes are considered.

On the other hand, the occurrence of the reactions in the solid phase and at low temperatures complicates the determination of their elementary rate constants. Under these conditions, the process kinetics depend on the rates of a number of physical stages, primarily diffusion, adsorption, and the dissolution of hydrogen atoms in the solid substance. In a more detailed approach one must take into account also the molecular motions in the solid phase; translation, rotations, etc.

The kinetic data obtained hitherto make it possible to infer the rate of interaction of hydrogen atoms with solid organic compounds as a whole and the rates of its individual stages. The kinetics of the reactions of atomic hydrogen at a low temperature are characterised by specific features associated with the manifestation of quantum effects. At low temperatures below a critical value T_{cr}, the rate of the reactions via the tunnel mechanism exceeds by a large factor the rate of the classical Arrhenius reaction. T_{cr} is proportional to the square root of the height of the potential barrier[79], so that at $T > 77$ K the tunnel effect is manifested most distinctly by reactions with large activation energies—the hydrogen atom transfer reactions. The following characteristics, which are the kinetic consequences of the transfer of a hydrogen atom via the tunnel mechanism, have been established for the $\mathrm{H} + \mathrm{HR} \rightarrow \mathrm{H_2} + \mathrm{R}$ reaction at 77–220 K: high rate constants at 80–100 K (10^{-19}–10^{-22} cm^3 s^{-1}), low effective activation energies at these temperatures ($<$ 1 kcal mole^{-1}), failure to obey the Arrhenius law, extremely large kinetic isotope effect when RH is replaced by RD, and a non-linear dependence of $\lg(k_{\mathrm{H}}/k_{\mathrm{D}})$ on $1/T$. One should note that the deviation from the Arrhenius law, due to the effect of the tunnel transfer of a hydrogen atom on the rate of the given reaction, is observed also at higher temperatures in the gas phase. However, the deviation at high temperatures is insignificant and can be observed only when kinetic data are analysed over an extended temperature range (300–1800 K)[100]. At a low temperature, the $\lg k - 1/T$ curves are distinctly concave (Figs. 7 and 8).

For reactions of atomic hydrogen with unsaturated compounds, the ratio of the rate constants for addition in two possible positions relative to the double bond of the olefin increases when hydrogen atoms are replaced by deuterium atoms. This isotope effect also indicates a tunnel mechanism of the addition reaction at a low temperature. Other kinetic manifestations of tunnelling, analogous to those described above, for hydrogen atom transfer reactions are to be expected at temperatures below 77 K, because the activation energy and hence also T_{cr} are lower for the addition reactions.

The studies of the kinetics of the interaction of atomic hydrogen with solid organic substances have established certain facts, which indicate a specific character of the chemical process in the solid phase. Thus the pre-exponential factor in the Arrhenius equation for reactions involving the addition of hydrogen atoms to unsaturated compounds (propene, polystyrene) and H + R reactions are smaller by 3 – 4 orders of magnitude than the collision number. Interesting data have been obtained concerning the pathways in the reactions of alkyl radicals with one another. Although recombination is energetically more favourable than disproportionation, alkyl radicals are destroyed in the solid phase mainly via a disproportionation mechanism and the ratio $k_{\text{disp}}/k_{\text{rec}}$ depends very markedly on the structure of the matrix.

After the manuscript had been sent to the printers, Ovchinnikova[103] published a study, in which the probabilities of tunnelling in the reaction $\mathrm{H} + \mathrm{H} - \overset{|}{\underset{|}{\mathrm{C}}} - \rightarrow \mathrm{H_2} + \overset{|}{\underset{|}{\dot{\mathrm{C}}}}-$ were calculated for a three-dimensional barrier. The exact quantum-mechanical solution of the problem was replaced by approximate calculations based on the classical S-matrix method. Comparison of the tunnelling probabilities for vibrational-adiabatic one-dimensional and three-dimensional barriers established that non-adiabatic effects significantly increase the probability of the tunnel reaction. Parameters of the model were selected for which the experimental data[28] (the dependence of the rate constant for the hydrogen transfer reaction on temperature and the isotope effects) agree with the results of the calculation.

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The α-Effect in the Chemistry of Organic Compounds

A.P.Grekov and V.Ya.Veselov

The anomalously high reactivity of compounds with one or several lone electron pairs at the atom adjoining the reaction centre (the α-effect) is discussed in relation to reactions involving nucleophilic substitution at the carbon atom in various valence states. The manifestation of the α-effect is noted for nucleophilic addition to a carbon atom; other examples of the α-effect in the chemistry of organic compounds are quoted. The possible causes of the effect are discussed, and a quantitative estimate of the latter is made.
The bibliography includes 234 references.

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I. INTRODUCTION

The report[1] describing the manifestation of the α-effect was published in 1955, but 1962, when Edwards and Pearson[2] first introduced the term "α-effect" and formulated its general characteristics, must be regarded as the date when research on this phenomenon began.

The α-effect is the term given to the anomalously high nucleophilic reactivity of many compounds having one or more pairs of lone electrons at an atom adjoining (i.e. in the α-position) a nucleophilic centre. Such compounds are hydrazine and its derivatives, hydroxylamine, hydroxamic acids, peroxide anions, the hypochlorite ion, etc. Epstein et al.[3] suggested that substances of this type can be referred to as α-nucleophiles and they are sometimes referred to in the literature as hypernucleophiles[4]. The α-effect is manifested as an appreciable positive deviation from the relation described by the Brønsted equation[5-7]:

$$\lg k = \beta\,pK + C\ .$$

The α-effect continues to attract the unflagging interest of chemists. The lack of a clear-cut understanding of the source of the high reactivity of α-nucleophiles led to numerous studies of reactions of different types, including reactions involving unsaturated and saturated carbon atoms[14-17]. The manifestation of the α-effect at nitrogen, phosphorus, sulphur, and peroxide oxygen atoms is being vigorously investigated[13,17-20]. A few years ago two reviews devoted to the α-effect were published[12,13], but they suffer from significant deficiencies: firstly, the numerous examples of the manifestation of the α-effect in organic chemistry are insufficiently covered, and, secondly, the reviews are somewhat obsolete, difficult to get hold of, and do not include the work of Soviet investigators.

The aim of the present review is to give a systematic account of the experimental observations of the α-effect in various processes in the chemistry of organic compounds, to discuss the possible causes of its manifestation, and to estimate it quantitatively. The review covers the literature up to 1976, that for 1977 is only partly included.

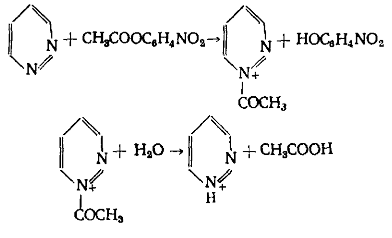
II. MANIFESTATION OF THE α-EFFECT IN THE CHEMISTRY OF ORGANIC COMPOUNDS

1. Nucleophilic Substitution Reactions at a Carbonyl Carbon Atom

Extensive data confirming the manifestation of the α-effect involving nucleophilic substitution reactions at a carbonyl carbon atom have now accumulated. In the reactions discussed below the α-effect has been studied in greatest detail.

(a) Reactions with carboxylate esters. Reactions involving the nucleophilic substitution of carboxylate esters by nucleophiles of different types have been investigated in fair detail; considerable factual data have accumulated concerning the manifestation of the α-effect, particularly in reactions with participation of aryl acetate esters[5,16,17,20-23]. Oximate anions[24] and hydroxamic[26-28] and *trans*-cinnamohydroxamic acid[29] exhibit an anomalously high reactivity in their reactions with 4-nitrophenyl acetate. The α-effect has also been observed in the reactions of 4-nitrophenyl thioloacetate with hydrazine in acetonitrile[30]. Analogous high reactivities have been noted in the interaction of benzohydroxamic acids and their *N*-methyl-substituted derivatives with phenyl acetate in 12% aqueous ethanol[31]. The ClO^- anion reacts with 4-nitrophenyl acetate twice as fast as the hydroxide ion, despite the fact that the latter is 10^9 times more reactive[16].

An anomalous reactivity is shown by certain heteroaromatic nitrogen-containing nucleophiles (pyridazine, phthalazine, and quinoline)[24,32]. Pyridine bases and diazines react with 4-nitrophenol acetate via a mechanism involving nucleophilic catalysis, which consists in the addition of a nucleophile to the substrate with formation of the *N*-acyl intermediate, which then rapidly hydrolyses[33,34]:



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In contrast to pyrazine, pyrimidine, and thiazole, pyridazine and isothiazole exhibit the α-effect in the interaction with 2,4-dinitrophenyl acetate[24,32]. The high reactivity of benzohydroxamic acids in reactions with 4-nitrophenyl benzoate and 4-nitrophenyl-4-nitrobenzoate has been demonstrated[35]. The α-effect has been noted in the hydrazinolysis and hydroxylaminolysis of the esters 8-acetoxyquinoline, 6-acetoxyquinoline, and 4-(2-acetoxyphenyl)imidazole[27].

In contrast to the aminolysis of esters[5,11,16,17,21], the reactions of hydrazine derivatives with arenecarboxylate esters are characterised by the absence of a catalytic effect both by a second molecule of the hydrazine derivative and by the reaction products[36-38]. The interaction of hydrazine derivatives with esters is greatly accelerated in the presence of small amounts of added carboxylic acids, amides, and tertiary amines; the rate constants for the reactions are linearly related to the catalyst concentration[37-40].

Table 1. The rate constants *k* (mole litre^{-1} s^{-1}) for the reactions of nucleophiles with chloroformates (in benzene at 25° C)[47-53].

Nucleophile	p*K*	Ethyl chloroformate	Phenyl chloroformate
$C_6H_5NH_2$	4.60	0.00374	0.183
$C_6H_5NHNH_2$	5.27	0.175	3.36
$C_6H_5N(C_2H_5)NH_2$	—	—	0.172
$C_6H_5CONHNH_2$	3.05	0.0510	1.33
$C_6H_5CON(CH_3)NH_2$	—	0.00576	0.174
$C_6H_5CSNHNH_2$	5.50	0.00410	0.0749
$C_6H_5CSN(CH_3)NH_2$	7.35	0.000721	0.150
$C_6H_5OCONHNH_2$	2.92	0.00752	0.196
$CH_3CONHNH_2$	3.24	0.0235	0.679
4-$CH_3C_6H_4SO_2NHNH_2$	1.41	—	0.00529
4-$CH_3C_6H_4SO_2N(n\text{-}C_3H_7)NH_2$	1.35	—	0.00114
$(CH_3)_2C{=}NO^-$	12.40	8.35	—

(b) Reactions with carboxylic acid anhydrides and chlorides. The study of the kinetics of the reactions of aroylhydrazines with carboxylic acid anhydrides and chlorides in benzene has revealed a high nucleophilic reactivity of aroylhydrazines compared with amines of the same basicity[41-46]. The interaction of acylhydrazines with carboxylic acid anhydride is complicated by the autocatalytic influence of the carboxylic acids evolved during the reaction[42-44]. An exception is the reaction of butyrylhydrazine with succinic acid anhydride; the product of this reaction is quantitatively separated from the reaction mixture and has no catalytic effect[44].

Amidoximes, which are hydrazine derivatives, exhibit the α-effect in reactions with chloroformates (chlorocarbonic acid chlorides) (Table 1), whereas in the reactions of arylamines with chloroformates an anomalous enhancement of nucleophilic reactivity has not been observed[53,54]. The reactions of chloroformates with hydrazine derivatives follow second-order kinetic equations for irreversible processes; the rate constants calculated from these equations remain satisfactorily constant during the process and are independent of the concentrations of the initial reactants[51,52,55-57]. Sulphonic acid hydrazines show a high reactivity in reactions with acryloyl chloride[58].

Separate Brønsted relations have been established for α-nucleophiles (hydrazine, acetylhydrazine, semicarbazide, thiosemicarbazide, hydroxylamine, and methoxyamine), on the one hand, and amines which do not show the α-effect, on the other, in reactions of nitrogen-containing nucleophiles with carbon dioxide[59].

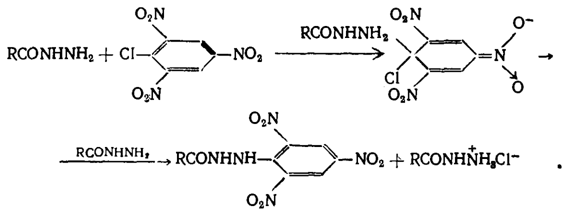
(c) Reactions with carboxylic acids. In the study of the kinetics of the reactions of hydrazine with glacial acetic acid at 25° C, Harris and Stone[60] established that the acylation of hydrazine is much faster than that of amines of similar basicity. The interaction of hydrazine and its substituted derivatives with certain carboxylic acids in oleum takes place via a series of transformations with formation of 2,5-disubstituted derivatives of 1,3,4-oxadiazole[61]; when hydrazine reacts with dibasic carboxylic acids in equimolar proportions, polyoxadiazoles are formed[62]. The condensation reactions of hydrazine and acylhydrazines take place satisfactorily only with aromatic carboxylic acids containing strong electron-accepting substituents (NO_2, COOH, etc.) in the ring[62,63]. The reaction with acids containing electron-donating groups is complicated by the sulphonation of the benzene ring by oleum[64,65].

In the condensation of acylhydrazines with carboxylic acids in *m*-cresol at 120–180° C the rate-determining stage is the slow formation of a cyclic complex between the reactants in the transition state, which decomposes with liberation of water and the formation of the corresponding acyl hydrazine[66-69]. The condensation of diacylhydrazines with dibasic acids takes place similarly and subsequently leads to the formation of polymers[64,65].

2. Nucleophilic Substitution Reactions at a Saturated Carbon Atom

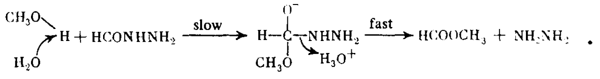
The first report of the α-effect in compounds with saturated carbon atoms is apparently that of Pearson and Edgington[14], who noted that benzyl bromide reacts with the HOO^- anion forty times faster than with HO^-. Benzyl bromide also exhibits a high reactivity in the reaction with neutral forms of amidoximes and *N*-methylhydroxamic acid[70]. The study of the reactivities of hydrazine, methoxyamine, and a number of different amines in relation to 1-halogeno-2,4-dinitrobenzenes in various solvents showed that hydrazine and methoxyamine exhibit small positive deviations from the Brønsted plot[71-74]. The halogen in 1-halogeno-2,4-dinitrobenzenes is quantitatively substituted by various amines, including α-nucleophiles; in terms of their reactivity, the halogens can be arranged in the sequence F > Cl > Br > I.[71-73] The reactivity of the hydrazine derivative diminishes with enhancement of the electron-accepting properties of the substituent. The same rule holds also in the reactions of picryl chloride with carboxylic and diarylphosphinic acid hydrazides[46,75].

The reactions of acylhydrazines with picryl chloride in benzene follow second-order kinetics. A mechanism has been proposed for the reactions involving the formation in the slow stage of an addition product (a quinonoid intermediate), which interacts with a second molecule of the initial hydrazine and is converted into the reaction product[76]:



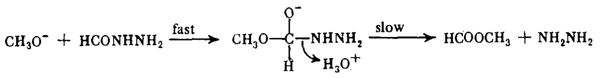
The absence of the α-effect in the reactions of hydrazine and hydroxylamine with alkyl iodides has been firmly established. However, the α-effect is manifested in the reaction of 1,8-naphthyridine with methyl iodide. In this case it is apparently necessary to take into account the geometrical disposition of the diamine heteroatoms (the nitrogen atoms with lone electron pairs are in the *peri*-positions) as a possible cause of the anomalous nucleophilic reactivity of 1,8-naphthyridine[32].

Formylhydrazine is more reactive in methanolysis than amides, which do not exhibit the α-effect[77]. At pH ≤ 5 methanolysis consists in the interaction of the reactants with the rate-determining formation of a tetrahedral intermediate, which then decomposes with the preferential formation of an ester and an amine:



$$\underset{H_2O}{\overset{CH_3O}{H}} + HCONHNH_2 \xrightarrow{slow} H-\underset{CH_3O}{\overset{O^-}{C}}-\underset{\searrow H_3O^+}{NHNH_2} \xrightarrow{fast} HCOOCH_3 + NH_2NH_2 \;.$$

This reaction undergoes general base catalysis. At pH > 9 the methanolysis of formylhydrazine involves the rate-determining decomposition of the intermediate into the reaction products[77]:



$$CH_3O^- + HCONHNH_2 \xrightarrow{fast} CH_3O-\underset{H}{\overset{O^-}{C}}-\underset{\searrow H_3O^+}{NHNH_2} \xrightarrow{slow} HCOOCH_3 + NH_2NH_2 \;.$$

An appreciable α-effect has been noted in the reactions of Malachite Green (tetramethyl-4-diaminotriphenylmethane) with hydrazine, methoxyamine, and CN^- and HOO^- ions.

3. Nucleophilic Substitution Reactions at a Phosphorus Atom

Systematic studies on the reactions of phosphate esters have revealed the α-effect for ClO^- and HOO^- ions, hydrazine, and hydroxylamine[82-86]. Isoproyl methylphosphonofluoridate ("Sarin", nerve gas) reacts with the HOO^- ion fifty times faster than with the HO^- ion[86,87-90] despite the fact that their basicity constants differ by a factor of 10^4 (Table 2). It has been noted that hydrazine and hydroxylamine exhibit an anomalous reactivity in the reaction with methyl 4-nitrophenylphosphate[91-93], 4-nitrophenyl phosphate[94], and 2,4-dinitrophenyl methyl phosphate[84,85] anions. The high reactivity of the methyl 4-nitrophenyl phosphate anion in the reactions with hydroxylamine and its *N*-alkyl substituted derivatives supports the occurrence of *O*-substitution and for certain compounds there is a possibility of the formation of a hydrogen bond with the phosphoryl oxygen, which is confirmed by the disappearance of the isotope effect[93].

Hydroximates are nucleophiles with an unusual reactivity in reactions with organophosphorus compounds[86,87,95]. The reactivity of various hydroximates and oximates in reactions with certain organophosphorus anticholinesterases is much higher than has been suggested on the grounds of their basicities[86].

Table 2. The rate constants k (litre $mole^{-1}$ min^{-1}) for the reactions of certain nucleophiles with phosphate esters[85,86].

Nucleophile	p*K*	Zarin	Tetraethyl pyrophosphate	2,4-Dinitrophenyl methyl phosphate
HO^-	15.27	2000	21	0.0505
HOO^-	11.60	94000	2180	10.4
ClO^-	7.4	600	267	—
NH_2OH	6.2	2.6	26	0.053
$C_6H_5CH_2NHO^-$	8.8	1020	160	—

4. Nucleophilic Addition Reactions

(a) Reactions with isocyanates. Nucleophiles can be arranged in the following sequence in terms of the rates of their reactions with isocyanates[96]: $AlkNH_2 > ArNH_2 > AlkOH > s\text{-}AlkOH \simeq H_2O > ArOH > RSH > RCOOH$; the position of *N*-substituted hydroxylamines in this series has not been established. It is known that the compounds RNHOH (R = Alk or Ar) react readily with isocyanates via the nitrogen atom, but, with increase of the electronegativity of the substituent, a tendency appears towards simultaneous *N*- and *O*-addition; *N*-substituted hydroxylamines are much more reactive than the corresponding amines in reactions with isocyanates[97]. This is due to the repulsion of the lone electron pairs of the adjacent electronegative atoms in hydroxylamines.

Phenyl isocyanate reacts with hydrazine derivatives in accordance with the following equation[98-109]:

$$R{-}NHNH_2 + O{=}C{=}N{-}R' \rightarrow R{-}NHNHCONH{-}R',$$
$$R = Ar,\ ArCO,\ AlkCO,\ ArSO_2,\ (Ar)_2PO,\ \text{or}\ (Ar)_2PS,\ R'{=}Ar.$$

It has been established that neither the initial reactants nor the products (substituted semicarbazides) influence the rate of reaction of hydrazine derivatives with phenyl isocyanate. The influence of substituents of different electronic types on the reactivity of hydrazine derivatives in reactions with phenyl isocyanate is described by the Hammett–Taft equation. In reactions of phenyl isocyanate with aliphatic acylhydrazines a separate correlation is observed for hydrocarbon groups and hydrogen, on the one hand, and the electronegative substituents, on the other, which is due to the different mechanisms of the effects of these substituents[99].

The enhanced reactivity of hydrazine derivatives in reactions with phenyl isocyanate (Table 3) is associated with the effect of the nitrogen atom of the imino-group adjoining the nucleophilic centre. It is believed that the α-effect in these reactions is due to the appreciable shift of the lone electron pair of the imino-nitrogen in the transition state and that an essential condition for the manifestation of the α-effect is the participation of the hydrogen atom of the imino-group in the formation of a hydrogen bond with the oxygen atom (or another electronegative atom) of the isocyanate[98-102,108]. The lower reactivity of hydrazine derivatives in reactions with phenyl isothiocyanate is apparently due to the difficulty of the formation of a hydrogen bond of the imino-group hydrogen–sulphur atom type in the transition state[108,109].

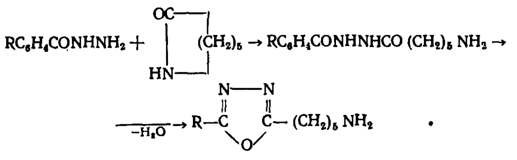
Kinetic studies of the synthesis of urea in the reactions of amines with cyanic acid showed that hydrazine is at least ten times more reactive than was believed on the grounds of its basicity and polarisability[110].

Table 3. The rate constants k (litre mole^{-1} s^{-1}) for the reactions of nucleophiles with phenyl isocyanate and phenyl isothiocyanate (in benzene at 25° C)[50,99-106].

Nucleophile	pK	Phenyl isocyanate	Phenyl isothiocyanate
$(C_6H_5)_2PONHNH_2$	3.02*	0.449	0,000411
$(C_6H_5)_2PON(C_2H_5)NH_2$	2,96*	0.0826	0.000184
$(C_6H_5O)_2PONHNH_2$	2.62*	0.140	0.0000867
$(C_6H_5O)_2PON(C_2H_5)NH_2$	2.51*	0,00534	0.0000203
$(C_6H_5O)_2PSNHNH_2$	2.70*	0,0878	0,0000958
$(C_6H_5O)_2PSN(C_2H_5)NH_2$	2,66*	0.0134	0.0000519
$C_6H_5NH_2$**	4.19*	0,00142	0.0000301
$C_6H_5NHNH_2$	5,27	1.09	—
$C_6H_5CONHNH_2$	3,05	1.92	—
$CH_3CONHNH_2$	3.24	0.614	—
4-$CH_3CH_4NH_2$**	5.12	0.00386	0.0000843
4-$CH_3C_6H_4SO_2NHNH_2$	1.41	0.0539	0,000396
4-$CH_3C_6H_4SO_2N(CH_3)NH_2$	1.36	0.00512	—
4-$CH_3C_6H_4SO_2N(n$-$C_3H_7)NH_2$	1.35	0,00397	—
$C_6H_5SO_2NHNH_2$	1.24	0,0432	—
$C_6H_5OCONHNH_2$	2,92	0.145	—
$C_6H_5N(C_2H_5)NH_2$	5.20	0.00777	—
$C_6H_5N(CH_3)NH_2$	4.99	0,00193	

*Measured in 50% aqueous ethanol.
**Quoted for comparison.

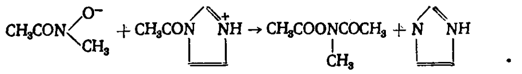
(b) **Reactions with ϵ-caprolactam.** The reactions of aroylhydrazines with ϵ-caprolactam at 160–270°C in *m*-cresol, decalin, and in the absence of solvents takes place via the following mechanism[111,112]:



The reactions of aroylhydrazines with ϵ-caprolactam in *m*-cresol solution are described by second-order kinetic equations for irreversible processes[111]. The interaction of benzoyl hydrazide, phenylhydrazine, semicarbazide, and carbohydrazide with ϵ-caprolactam in *m*-cresol take place in 10–20 h at 250° C, while in the presence of aniline appreciable changes are not observed even after 100 h.[113] The introduction of small amounts of primary and tertiary amines as well as carboxylic acid derivatives does not affect the rate of reaction of ϵ-caprolactam with benzoylhydrazine, while carboxylic acids themselves, which behave as bifunctional catalysts, accelerate the process[111,112].

5. Other Instances of the Manifestation of the α-Effect

NN-Dialkylhydroxylamines react faster with t-butyl peroxide than do other dialkylamines, which is used in the synthesis of nitrenes[114]. The rate constants for the reactions of hydrazine and hydroxylamine with 4-nitrophenyl sulphate are several times greater than those for the reactions with amines of similar basicity[117]. The α-effect has been observed in the reaction of *N*-acetyl-*N*-methylhydroxylamine with acetylimidazole[115]:



The anomalous reactivity of acetylimidazole in the hydrazinolysis[116-118] and methoxyaminolysis of *N*-acetyltriazole[116] and of 2-acetyl-3,4-dimethylthiazolium iodide in the reaction with hydroxylamine (in contrast to imidazole, which has a similar basicity but is relatively unreactive) has been pointed out[119]. The inapplicability of the Brønsted relation between the logarithm of the reaction rate constant and the basicity/acidity of the catalyst to the acid- and base-catalysed hydrolysis of 4-tolyl *NN*-dimethylacetimidate has been demonstrated[116].

The reactions of δ-thiovalerolactone with hydrazine and morpholine undergo general acid and base catalysis[120]. The hydrazinolysis of δ-thiovalerlactone is much faster than the morpholinolysis of the same thiester, which is due to the α-effect[121].

Two-centre nucleophiles (hydrazine, hydroxylamine, and their derivatives) exhibit an enhanced reactivity in reactions with heterocycles containing polar double bonds ($C = X$, where $X = O$, S, N, or P) compared with one-centre nucleophiles (ammonia, primary amines, 1,1-disubstituted hydrazines, and sulphide and hydroxide ions, for example)[122]. The α-effect can have a significant influence on the rate-determining stage of the recyclisation reaction and can affect the mode of the rearrangement; furthermore, two-centre nucleophiles can react via one or two heteroatoms in the ring rearrangement process[122].

The α-effect has been noted in reactions involving the nucleophilic addition of aliphatic 1,1-dinitrocarbanions to methyl acrylate and methyl vinyl ketone in water and 50% aqueous dioxan (the Michael reaction)[123,124]. The virtual equality of the Brønsted β-constants for the addition reactions involving methyl acrylate and methyl vinyl ketone and the recombination of the carbanion with a proton as well as the identical enthalpies of activation for the above reactions indicate the existence of a common stage associated with the localisation of the charge at the carbon atom of the dinitro-carbanion when the hybridisation of this atom changes from sp^2 to sp^3.[124] The rate of the Michael reaction in water at 30°C is 3400 times higher (4200 times higher in 50% aqueous dioxan) for carbanions with $R = F$ than for carbanions with $R = CH_3$ or C_2H_5, which is apparently due to the repulsion of lone pairs of p electrons of the fluorine atom and the carbanion carbon (i.e. the destabilisation of the sp^2-hybridised carbon by the fluorine atom in the α-position)[124].

A series of carbanions derived from *N*-substituted 1,1-dinitroacetamides, i.e. $RNHCOCH(NO_2)_2$, are characterised by an anomalous reactivity in nucleophilic addition to methyl vinyl ketone via the Michael reaction in water and methanol in the temperature range 10–50° C; the operation of the α-effect in these reactions is demonstrated by the authors by the analysis of the influence of various structural factors on the nucleophilic properties in terms of the linear free energy equations[125].

The rate of ferrocenylmethylation of aliphatic 1,1-dinitrocarbanions in 50% aqueous methanol at 45–60° C is independent of the basicity of the anions derived from 1,1-dinitroalkanes[126]. The high rate of ferrocenylmethylation and the absence of *O*-alkylation of dinitro-carbanions are probably due to the influence of the α-effect. The study of the kinetics of the reactions of ferrocenylmethylpyridinium salts with mono- and di-nitro-carbanions permitted a soundly based approach to the selection of the optimum conditions for the preparative synthesis of β-nitro- and $\beta\beta$-dinitro-alkyl derivatives of ferrocene.

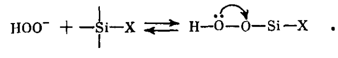
The interaction of platinum(II) complexes with hydrazine, hydroxylamine, acid anions, ammonia, and pyridine takes place in two stages; the first stage is slow and rate-determining[127,128]:

$$trans\text{-}[PtL_2Cl_2] + Y \xrightarrow{\text{slow}} trans\text{-}[PtL_2ClY] + Cl^-,$$

$$trans\text{-}[PtL_2ClY] + Y \xrightarrow{\text{fast}} trans\text{-}[PtL_2Y_2] + Cl^-,$$

where L is an organic ligand, which may be pyridine, piperidine, or $P(C_2H_5)_3$, and Y is a nucleophile. The nucleophilic reaction constants for bivalent platinum in the reactions with hydrazine and hydroxylamine are much higher than in the reactions of the complexes with pyridine, ammonia, and NO_2^- and N_3^- ions; the latter implies that the α-effect is responsible for the much greater reactivity of α-nucleophiles compared with other nitrogen-containing compounds[127,128].

Hydrazine, hydroxylamine, and the HOO^- ion show a much greater reactivity than have been suggested in reactions with the octahedral tris(acetylacetonato)silicon(IV) cation[129]. The high reactivity of such nucleophiles is attributed to the influence of the α-effect, which is manifested by the fact that the lone electron pairs stabilise the transition state, compensating thereby the loss of electrons by the nucleophilic atom[1]:

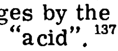


$$HOO^- + -\overset{|}{\underset{|}{Si}}-X \rightleftarrows H-\ddot{O}-\ddot{O}-Si-X\ .$$

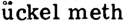
The interaction of the reactants is promoted by the high positive charge on the silicon atom and the unfilled outer *d* orbitals of the tris(acetylacetonato)silicon(IV) cation[129]. Sander and Jencks[130] pointed out the extremely high reactivity of the HOO^- ion in its reactions with acetaldehyde and formaldehyde.

The experimental data on the reactivities of α-carbofunctional compounds of Group IVB elements, the "mesoids" $\gt M-\overset{|}{\underset{|}{C}}-X$ (where M = Si, Ge, or Sn, i.e. elements having atoms with vacant *d* orbitals; H = Hal, N, O, or S), as well as studies by infrared, NMR, and NQR spectroscopy and other physical methods indicate the anomalous behaviour of the above compounds[131,132]. The ^{35}Cl frequencies in the NQR spectra of mesoids confirm that the mechanism of the transmission of the electronic influences for M = Si, Ge, or Sn differs appreciably from the purely inductive effect for M = C; together with the inductive effect, there is intramolecular coordination between M and X atoms[132]. If M has vacant *d* orbitals, the ^{35}Cl frequency is higher than for the corresponding organic analogue (i.e. for M = C).[133] If M is an atom with lone-pair electrons, then the ^{35}Cl frequency proves to be lower. A more detailed analysis of the NQR spectra of compounds of this type led to the conclusion that the regularity in the variation of the frequencies is associated primarily with the electronegativity of the M atom. The ^{35}Cl NQR spectra of all chloroderivatives of nitrogen-containing heterocyclic compounds exhibit the above regularity[134]. The appreciably different ^{35}Cl frequencies of the NQR spectra when the chlorine atoms are in the α-positions relative to the nitrogen atoms of the pyridine and pyrrole types in 3-substituted 5-chloro-1,2,4-triazoles are due to the electronegativity of the nitrogen atoms[135].

The high reactivity of the halogen atom (chloromethyl) in alkyl esters compared with the corresponding alkyl halides has been frequently interpreted from the standpoint of the electronic theory. The anomalously low ^{35}Cl frequencies are attributed[136] either to the interaction between the lone electron pair of the oxygen atom and the σ electrons of the C–Cl bond (I) or to the formation of an intramolecular three-centre bond (II):

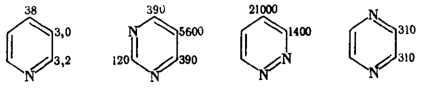


(I)

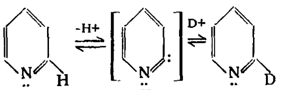


(II)

Zoltewicz et al.[137] demonstrated the non-equality of the rates of isotopic H–D exchange for different positions in the heteroaromatic pyridine, pyrimidine, pyridazine, and pyrazine rings (the numerals indicate the second-order rate constants at 164.6° C, multiplied by 10^6, measured in a CH_3OD-CH_3ONa medium):



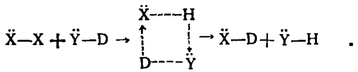
Positions which are either adjacent to the nitrogen atom or are located between two nitrogen atoms show the smallest capacity for H–D exchange. The base-catalysed deuterium exchange involving pyridine takes place most readily in the 4-position[138], although, according to calculations of the charges by the Hückel method, the 2-position, should be the most "acid".[137] Calculations by the extended Hückel method show that the 2-carbanion of pyridine is destabilised by the influence of the lone-pair electrons[138]. The loss of stability by the heterocycle is due to the intermediate (or transition) state (III), the formation of which accompanies proton transfer from a position adjoining the nitrogen atom[13]:



(III)

The reduced reactivity of α-carbon atoms in isotope exchange reactions is the result of the operation of two factors: the decrease of the *s*-character of the hydrogen bond with the carbon atom adjoining the nitrogen atom of the nucleophile and the repulsion between the electron pairs of the nitrogen and the carbanion generated[137,141].

Mention should be made of the α-effect in the exchange of hydrogen for the deuterium of heavy water in ammonia, ammonium salt, and sucrose solutions[142]. The capacity of hydrogen for exchange depends on the nature of the bond; in hydrogen bonds with halogens, oxygen, nitrogen, sulphur, selenium, and other elements having lone-pair electrons the exchange takes place very readily and in many instances instantaneously. The exchange of hydrogen in C–H bonds is as a rule very difficult and may be accelerated only in the presence of strong bases, which promote the abstraction of a proton, in the presence of strong acids, which facilitate the transfer of deuterium, or, finally, in the presence of suitable substituents which weaken the C–H bond. Deuterium exchange takes place in the reaction complex (**IV**) formed via hydrogen bonding ($\ddot{X}$ and $\ddot{Y}$ are atoms or parts of molecules):



$$\ddot{X}-X+\ddot{Y}-D \rightarrow \begin{matrix}\ddot{X}\text{----}H\\ \uparrow \quad\quad \downarrow\\ D\text{----}\ddot{Y}\end{matrix} \rightarrow \ddot{X}-D+\ddot{Y}-H \quad .$$

(IV)

The maximum rate of the alkaline hydrolysis of the haloforms CHX_3 (X = Hal) is a phenomenon common to all halogenomethanes[143,144]. For example, the rate of hydrolysis of $CHCl_3$ is one thousand times higher than that of CH_2Cl_2 and the rate of hydrolysis of bromine-containing haloforms is higher by approximately three orders of magnitude compared with CH_2ClBr or CH_2Br_2. Carbenes are intermediates in the alkaline hydrolysis of haloforms; 1,1-elimination takes place via the mechanism involving unimolecular elimination from the conjugate base:

$$CHX_3+HO^- \rightleftarrows CX_3^- + H_2O \quad ,$$
$$CX_3^- \rightleftarrows :CX_2+X^- \quad ,$$
$$:CX_2+H_2O \xrightarrow{HO^-} CO+HCOO^-+X^- \quad .$$

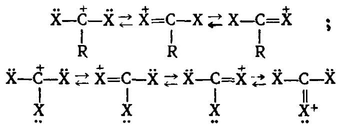
The introduction of a fluorine atom into the haloform has the most appreciable kinetic effect compared with other halogens. Difluoromethanes (CHF_2Cl, CHF_2Br, CHF_2) are hydrolysed much faster, which conflicts with the suggested mechanism. Hine[143-145] interprets these results on the hypothesis of a single-stage bimolecular 1,1-elimination mechanism:

$$HO^-+H-CF_2X \rightarrow H_2O+CF_2+X^- \quad ,$$
$$CF_2+H_2O \xrightarrow{HO^-} CO+HCOO^-+F^- \quad .$$

The electron shift from the heteroatom to the electron-deficient carbene carbon has a significant influence on the reactivity of carbenes containing α-heteroatoms with lone-pair electrons. If the heteroatom is linked by a double bond to the carbene carbon, then the shift of electron density leads to the formation of stable compounds such as isonitriles and derivatives of fulminic acid and carbon monoxide[145]; these compounds do not exhibit electrophilic properties and behave as more or less reactive nucleophiles. The carbene ions are stabilised by the lone-pair electrons of the heteroatom X in the α-position relative to the cationic centre[46-148]:

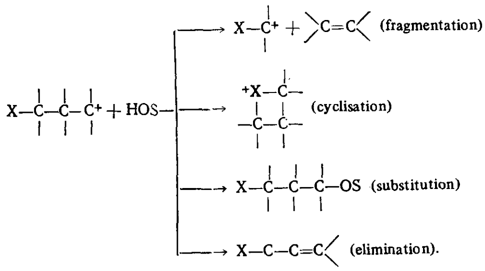
$$R_2\overset{+}{C}-\ddot{X} \rightleftarrows R_2C=\overset{+}{X},\ X=\text{Hal, N, O, S, or Se} \quad .$$

The stabilising effect increases sharply if the electron-deficient carbon atom is linked to two or even three electron-donating heteroatoms X[147]:



$$\ddot{X}-\underset{R}{\overset{+}{C}}-\ddot{X} \rightleftarrows \overset{+}{X}=\underset{R}{C}-X \rightleftarrows X-\underset{R}{C}=\overset{+}{X} \quad ;$$
$$\ddot{X}-\underset{\ddot{X}}{\overset{+}{C}}-\ddot{X} \rightleftarrows \overset{+}{X}=\underset{\ddot{X}}{C}-\ddot{X} \rightleftarrows \ddot{X}-\underset{\ddot{X}}{C}=\overset{+}{X} \rightleftarrows \ddot{X}-\underset{\ddot{X}^+}{\overset{}{C}}-\ddot{X} \quad .$$

The stability of the carbonium ion formed in the solvolysis of precursor carbonium ions is exceptionally high in those cases where the atom adjoining the carbonium centre has lone-pair electrons, the symmetry of the orbitals of which is favourable for overlapping with the vacant *p* orbital of the carbonium centre. Solvolysis of carbonium ions containing α-substituents with lone-pair electrons is accompanied by mutually competing reactions[149,150] (HOS is the solvent):



III. DEPENDENCE ON THE NATURE OF THE REACTANTS

Since the dependence of the α-effect on the nature of the reactants has been analysed in detail in a review[13], in this section we shall consider examples where the α-effect loses its force (vanishes). Epstein et al.[3] suggested a close relation between the manifestation of the α-effect and the nature of the nucleophile and the substrate involved in the reaction. Together with the above examples of the reactions where the α-effect has been noted for hydrazine and its derivatives, data have been obtained on reactions in which hydrazine does not show an enhanced reactivity[151,152]. Thus, whereas the α-effect is possible in the interaction of 4-nitrophenyl acetate with hydrazine and methylhydrazine, *NN*-dimethylhydrazine does not exhibit a high reactivity; the point corresponding to the above nucleophile fits on the linear Brønsted plot for primary and secondary amines[8].

The α-effect has been demonstrated for reactions of hydrazine, hydroxylamine, sulphides, and other nucleophiles with methyl iodide in methanol[126]; on the other hand, an anomalous reactivity of this substrate has not been observed in the interaction with hydrazine, hydroxylamine, and their monomethyl derivatives in an aqueous medium[15]. Gregory and Bruice's paper[15] was perhaps the first report on the α-effect in the reaction of neutral nucleophiles with saturated substrates. The α-effect has not been observed in the reactions of alkyl iodides with hydrazine in acetonitrile[152], methyl iodide does not exhibit an enhanced reactivity in reactions with heteroaromatic nitrogen-containing nucleophiles (including pyridines, diazines, and their analogues) in dimethyl sulphoxide at 23°C.[32] Hydrazine and methoxyamine react with 1-chloro-2,4-dinitrobenzene, showing very insignificant α-effects[71].

Systematic studies on the nucleophilic reactions of phosphate esters revealed the α-effect for hydrazine and hydroxylamine[84,85]. However, there is no α-effect in the reactions of the monoanion of 4-nitrophenyl methylphosphonate with hydrazine; other nucleophiles show a very insignificant α-effect in their reactions with this substrate[91-93]. The differences between the reactivity of hydrazine, which behaves as a neutral reactant in these processes, and those of other α-nucleophiles are extremely insignificant[88]; the α-effect has not been noted in the hydrazinolysis of phosphate esters[94].

α-Nucleophiles incapable of participating in the formation of a transition state characteristic of the push-pull mechanism have the "normal" reactivity[8,16,153]. Certain amidoximes react very slowly with Sarin and di-isopropyl phosphorofluoridate; *N*-triphenylmethylhydroxylamine does not react with these substrates at all[154]. The α-effect has not been observed in the interaction of nitroethane with hydrazine, methylhydrazine, hydroxylamine[151], and alkyl iodides[32,153]; this demonstrates in the first place, a close relation between the α-effect and the type of transition state (more precisely Brønsted's β constant). By analogy with proton transfer reactions[15,155], the high values of β should be attributed largely to the intense bond formation in the transition state. However, according to Hammond's postulate[156], this analogy is not altogether correct.

There is no α-effect in the reactions of *NN*-dimethylhydrazine with 2-phenyl-L-4-benzyloxazolone[10], which can be accounted for by the impossibility of the formation of a hydrogen bond with the carbonyl oxygen.

In the deprotonation of t-butylmalononitrile all nucleophiles (including hydrazine, hydroxylamine, methoxyamine, and peroxide ions) show the "normal" reactivity and fit on a single common Brønsted linear plot[155,157]. The α-effect has not been noted in the reaction of 1-chloro-2,4-dinitrobenzene with hydrazine and methoxyamine[46] and of picryl chloride with carboxylic acid hydrazides[50], *N*-alkyl-*N*-arylhydrazines[50], and phosphorus acid hydrazides and their *N*-ethyl-substituted derivatives[104].

The cause of the absence of the α-effect in the reactions of 2,4-dinitrophenyl acetate with pyridine and pyridazine at 25°C in water is not clear[5,33,158]. This example is particularly surprising, since strong interaction of the unpaired electrons of the two nitrogen atoms in the above nucleophiles has been demonstrated and confirmed by molecular orbital calculations[159] and photoelectron spectra[160].

The above example makes it clear that the α-effect depends both on the type of substrate and on the nature of the nucleophile. Fairly convincing experimental data have now accumulated, showing that the α-effect of the substrate depends primarily on the valence state of the carbon atom and can be arranged in the following sequence: $sp > sp^2 > sp^3$. This behaviour is illustrated quantitatively by the ratios $k_{\mathrm{HOO^-}}/k_{\mathrm{HO^-}}$ and the rate constants for the reactions with bromophenylacetic acid, 4-nitrophenyl acetate, and benzonitrile, which indicate different values of the α-effect due to the carbon atoms in different valence states[161]. It is suggested that the α-effect of the carbon atom is enhanced with increasing *s*-character of the bonding orbitals[152].

IV. THE POSSIBLE CAUSES OF THE α-EFFECT

The possible causes of the α-effect have now been established and analysed[8,128], the main ones being as follows: destabilisation of the ground state of the nucleophile due to the electrostatic repulsion between the electrons of adjacent electronegative atoms[32,162]; stabilisation of the transition state owing to the overlapping of the lone-pair electron orbitals[12,13]; reduced solvation of α-nucleophiles compared with reactants which do not exhibit the α-effect[15,163,164]; stabilisation of the reaction products (this factor also stabilises the transition state[79,115,165]); polarisability of the transition state[163]. During recent years several new causes of the α-effect have been added to the above list[4]. Certain probable causes of the α-effect are discussed in detail below, but any one of them in isolation does not fully account for the nature of this phenomenon.

1. Destabilisation of the Ground State

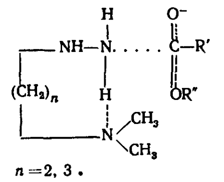
The first hypothesis of the destabilisation of the ground state of the nucleophile as a possible cause of the anomalous reactivity was put forward as early as 1962.[162] The α-effect in hydrazine derivatives may be due to the difference between the free energies of the ground states of the initial reactants and the reaction products[32,79,166]. The energy of the ground state increases owing to the electrostatic repulsion between the electrons of adjacent electronegative atoms[8,162]. This conclusion is confirmed by the photoelectron and EPR spectra of substituted hydrazines[167-170]. The repulsion of the lone-pair electrons in molecules of the type H_2O_2, NH_2NH_2, HClO, and ClF[171-174] introduces serious errors into estimates of the enthalpies of reaction and heats of dissociation of the adducts of Lewis acids and bases by the Drago–Wayland equation and leads to values of these quantities which are appreciably too low[175,176]. The repulsion of the electron pairs is responsible for the inaccurate prediction of the bond lengths and heats of formation of α-nucleophiles; the calculated bond lengths are too small and the heats of formation evaluated from the incorrect bond lengths are negative[177].

The increase of the energy of the ground state acts in the same direction as the decrease of the activation energy, which leads to an increase of the rate constants; however, the repulsion of the lone-pair electrons should also lead to an increase of basicity. The simultaneous increase of the rate constants and basicity should not apparently result in the appreciable lack of correspondence between basicity and reactivity observed experimentally[8]. In hydrazine and its derivatives the electrostatic repulsion between the lone-pair electrons of the nitrogen atoms diminishes in the transition state owing to the decrease of the charge of the nitrogen atom of the amino-group, the lone-pair electrons of which are involved in conjugation with the bond being formed, stabilising thereby the transition state[178,179]. Furthermore, such conjugation is the cause of the increase of the ability of the NH bridge group in monosubstituted hydrazines to transmit electronic influences in reactions with carbonyl-containing substrates ($z_{\mathrm{NH}} \simeq 1$).[51,99,104] The low N–X, O–X, and F–X bond energies are attributed to the influence of the repulsion of the lone-pair electrons in the ground state (X is an electronegative atom), the weakening of the above bonds becoming more pronounced with increase of the electronegativity of X.[180]

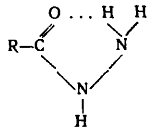
2. Stabilisation of the Transition State

The stabilisation of the transition state may be due to general intramolecular base catalysis and resonance interaction. Epstein et al.[3] proposed acid–base mechanisms for reactions involving nucleophilic attack on esters (particularly with formation of hydrogen bonds); similar mechanisms are discussed in later communications[158,182,183]. Bifunctional catalysis and resonance stabilisation have been examined by Jencks[158].

(a) General intramolecular base catalysis. The rate constants for the reactions of 2-dimethylaminoethylhydrazine and 3-dimethylaminopropylhydrazine with phenyl acetate are one thousand times higher than would be expected on the grounds of their basicity[184]. The high reactivity of dimethylaminoalkylhydrazines is due to the general intramolecular base catalysis [see formula (V)]:



(V)



(VI)

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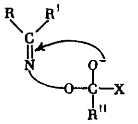
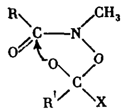
The occurrence of the catalysis illustrated by formula (V) is confirmed by the dependence of the rate constants on the concentration of the dimethylamino-group in the form of the free base[184].

The increased reactivity of carboxylic acid hydrazides in reactions with carbonyl-containing substrates can be explained by general intramolecular base catalysis involving the formation of an intramolecular hydrogen bond of type (VI). The formation of such intramolecular bonds is indicated by the shift of the ν(C=O) and ν(N–H) stretching vibration frequencies in the infrared spectra of carboxylic acid hydrazides[185,186], the measured dipole moments[187], and the study of the structure of the hydrazide group by the CNDO/2 method[188]. The replacement of the oxygen atom of the carbonyl group by the less electronegative sulphur atom leads, on the one hand, to an increased basicity of the amino-group and, on the other hand, to a decrease of the mobility of the hydrogen atoms of the amino-group, which hinders the formation of an intramolecular hydrogen bond; the latter is the most likely cause of the reduced reactivity of thiobenzoylhydrazine[32,48]. Phenoxycarbonylhydrazine, in which an intramolecular hydrogen bond of type (VI) has not been observed[185], exhibits a much lower reactivity compared with benzoylhydrazine despite the similarity of their basicity constants[48,99]. Evidently general intramolecular base catalysis has some effect on the reactivity of hydrazine and its derivatives. However, on the basis of this hypothesis, it is impossible to explain the lower reactivity of N-benzoyl-N-methylhydrazine in the reactions with ethyl chloroformate[48], phenyl chloroformate[50-52,55], and esters[38] as well as the absence of an increase in the reactivity of hydrazine derivatives in reactions with picryl chloride[46,75]; general intramolecular base catalysis should operate in the above reactions, because the presence of N-methyl groups does not apparently affect its occurrence[184].

The manifestation of the α-effect in the acylation of neutral amidoximes[57] and oximate anions with 4-nitrophenyl acetate (VII) can be accounted for by general intramolecular base catalysis[9]. The α-effect in N-methylhydroxamic acids has been explained by a similar mechanism (VIII):[189]



(VII)



(VIII)

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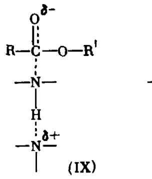
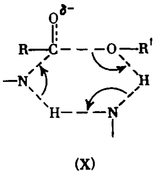
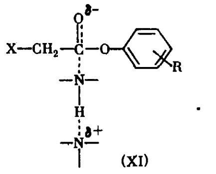
Bruice et al.[183] showed that the aminolysis of esters can also involve general base catalysis (IX–XI):



(IX)



(X)



(XI)

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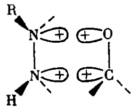
The delocalisation of the negative δ-charge on the carbonyl oxygen atom corresponds to scheme (IX), a cyclic proton transfer corresponds to scheme (X), and the localisation of the δ-charge on the phenolic oxygen atom corresponds to scheme (XI).

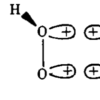
The high reactivity of hydrazine in reactions with the esters 4-(2-acetoxyphenyl)imidazole, 6-acetoxyquinoline, and 8-acetoxyquinoline is due to the fact that the adjoining imidazole group promotes a high rate of reaction of the reactants, behaving as a general intramolecular base catalyst; under the same conditions, phenyl acetate reacts with hydrazine forty times more slowly than with 6-acetoxyquinoline[27].

(b) The formation of an aromatic transition state. Liebman and Pollack[190] proposed an explanation of the α-effect based on allowance for the interaction of the electron pair orbitals in the transition state, which does not occur either in the initial reactants or in the products. This interpretation of the α-effect takes into account the fact that a high reactivity is observed only for substrates with π orbitals and provides a much better interpretation of the increase of reactivity than could be achieved by analysing the stability of the reaction products.

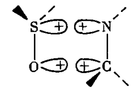
By means of this approach, it has been shown that the addition of hydrazine to the carbonyl group leads to the formation of a six-electron aromatic transition state (XII); a transition state of an analogous type is probably formed as a result of the addition of the peroxide ion to benzonitrile (XIII) and of bisulphite to oximes (XIV)[177]:



(XII)



(XIII)



(XIV)

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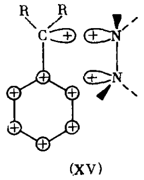
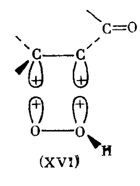
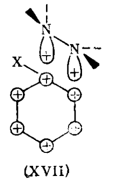
The α-effect in reactions involving the addition of α-nucleophiles to Malachite Green[78,79] can be explained by the formation in the course of the reaction of a cyclic transition state with aromatic properties. If Malachite Green is regarded as a substituted benzyl cation, then (XV) can be treated as a transition state incorporating ten electrons, as a result of which the system acquires aromatic properties[190]:



(XV)



(XVI)



(XVII)

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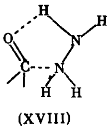
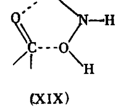
The addition of peroxide ions in the Michael reaction[121,122] and the transition states in aromatic nucleophilic substitution reactions are illustrated in structures (XVI) and (XVII)[190].

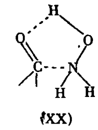
Hydrazine and its derivatives are capable of bifunctional (electrophilic-nucleophilic) interaction with carbonyl-containing substrates (esters, acid halides, acylureas, anhydrides, and oxazolinone). The transition states in the above reactions are illustrated by scheme (XVIII)–(XXI)[10]:



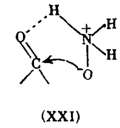
(XVIII)



(XIX)



(XX)



(XXI)

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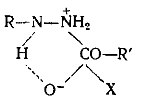
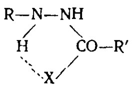
The reaction of oxazolinone with hydroxylamine involves competition between the oxygen and nitrogen atoms in which there is a bifunctional attack on the neutral hydroxylamine molecule [(XIX)–(XX)]. In addition one cannot rule out the possibility of attack by the oxygen atom in the form of the zwitter-ion (XXI); the last scheme explains the formation of a considerable amount of *O*-acyloxazolinone[10]. Epstein et al.[89] describe the appearance of stable transition states in the reactions of Sarin and the ClO^- ion with various phosphorus-containing substrates.

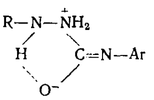
An aromatic transition state in the reactions of monosubstituted hydrazines with carbonyl-containing substrates is formed via a hydrogen bond between the oxygen atom (or another electronegative atom) and the hydrogen atom of the imino-group and via a new bond between a carbon atom of the substrate and the amino-group of the nucleophile. The transition state is of type (XXII) for reactions of monosubstituted hydrazines, of type (XXIII) for reactions with benzoyl chloride[41,50], phenyl chloroformate[51,52], and carboxylate esters[38], and of types (XXIV) and (XXV) for reactions with phenyl isocyanate[99,100]:



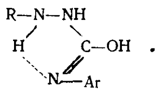
(XXII)



(XXIII)



(XXIV)



(XXV)

The formation of structures (XXII)–(XXV) is favoured by the disposition in a single plane of the hydrogen atom of the imino-group and the lone-pair electrons of the amino-nitrogen[191]. Furthermore, the aromatic transition state promotes a more complete shift of electron pair from the nucleophilic centre and is energetically the most favourable[190,192]. Convincing arguments involving cross-correlation analysis have been put forward for the possibility of the formation of transition states of types (XXII) and (XXIII) in the acylation of carboxylic acid hydrazides by aryl chloroformates and aroyl chlorides[41,52,55].

The hypothesis of the formation of transition states of type (XXII)–(XXV) in reactions of monosubstituted hydrazines with carbonyl-containing substrates is also supported by the kinetic parameters of the reactions with *NN*-disubstituted hydrazines. The replacement of a hydrogen atom in the imino-group by an alkyl substituent eliminates the possibility of the formation of an aromatic transition state, which leads to a decrease of the reactivity of *NN*-disubstituted hydrazines[50,104]. It is clear from the foregoing that, when monosubstituted hydrazines react with carbonyl-containing substrates, there is a possibility of the formation of transition states (XXII)–(XXV) with a high stability. Consequently the α-effect is shown by hydrazine derivatives on interaction with substrates containing π orbitals; the transition states in these reactions are aromatic and contain $4n + 2$ electrons.

By virtue of the specific features of the nucleophilic substitution at an aromatic carbon atom, the formation of transition states (XXII)–(XXV) is impossible in reactions with picryl chloride; the mechanism of such reactions involves the formation of intermediates having quinonoid structures[75]. Presumably this factor is the main cause of the low reactivity of hydrazine derivatives in reactions with picryl chloride.

3. Differences in Solvation Effects

Solvation is not one of the main causes of the α-effect, but the accumulated factual data do not allow neglect of this factor[165,193,194]. It is suggested that α-nucleophiles are much less solvated than other nucleophiles, which do not show the α-effect. This question has not been completely worked out in detail, the interpretation of certain solvation effects still does not fit satisfactorily within the framework of generally accepted theories, and experimental results are difficult to account for in many instances. Furthermore, solvation is one of the destabilising factors which should alter both the basicity and the nucleophilic reactivity of the compound[158]. The nucleophilic properties of hydrazine in acetonitrile in the reaction with 4-nitrophenyl acetate, for example, are much more marked than would follow from the pK value and this is why in an aprotic solvent, such as acetonitrile, hydrazine exhibits the α-effect[15].

Benzamidine (pK = 11.6) reacts with 4-nitrophenyl acetate in chlorobenzene approximately 15 000 times faster than does n-butylamine (pK = 10.6) despite the small differences between the basicity constants[192]. In a study of the reactions of peroxide ions with benzonitriles, Wiberg[163] stated that the HOO^- ion is approximately 10^4 times more reactive than the HO^- ion. The differences between the reactivities cannot be attributed to the low enthalpies of activation and differences between the entropies of activation; this fact should probably be explained by the influence of the solvent (a 50% aqueous acetone solution was used). The reactions of peroxide ions with benzonitriles, which have been studied in detail[161,195], are greatly influenced by solvation[196].

Table 4. The rate constants k (litre $mole^{-1}$ s^{-1}) for the reactions of phenyl isocyanate with certain nucleophiles in various solvents at 25° C[102,103,107] (*DN* is the donor number of the solvent[198]).

Solvent	*DN*	Diphenylphosphinic acid hydrazide	4-Tosylhydrazine	4-Toluidine
Hexamethylphosphoramide	38.8	—	—	0.436
Pyridine	33.1	8.84	—	—
Diethylacetamide	32.2	7.11	—	—
Dimethyl sulphoxide	29.8	7.24	3.57	0.164
Dimethylacetamide	27.8	5.50	1.88	0.0784
Dimethylformamide	26.6	4.90	1.64	0.0601
Tetrahydrofuran	—	3.00	1.25	—
Dioxan	—	2.74	0.923	—
Diethyl ether	19.2	2.63	0.723	0.0347
Ethyl acetate	17.1	2.14	—	0.0315
Methyl acetate	16.5	2.07	—	—
Acetonitrile	14.1	1.72	—	—
Nitrobenzene	4.4	0.727	0.163	0.00697
Benzene	0	0.449	0.0539	0.00397

A parallel relation between the logarithms of the rate constants and the donor numbers (*DN*) of the solvents (Table 4), described by Eqn. (1) for reactions with diphenylphosphinic acid hydrazide[197] and by Eqn. (2) for reactions with tosylhydrazine[103,199], has been demonstrated for the reactions of phenyl isocyanate with certain hydrazine derivatives:

$$\lg k = -0.294 + 0.0372\,DN \quad (r = 0.997), \tag{1}$$

$$\lg k = -1.12 + 0.049\,DN \quad (r = 0.989)\ . \tag{2}$$

For the reactions of phenyl isocyanate with 4-toluidine (which does not exhibit the α-effect), the influence of solvents on the reactivity of nucleophiles should be described by the following equation:

$$\lg k = -2.67 + 0.050\,DN \ (r = 0.987) \ . \qquad (3)$$

The study of the influence of donor solvents in a mixture with benzene on the rate of reaction of phenyl isocyanate with hydrazine derivatives showed that even small amounts of added donor solvents increase significantly the rate of reaction. A linear relation, described by Eqn. (4) for diphenylphosphinic acid hydrazide[197] and by Eqn. (5) for tosylhydrazine[103], holds between the logarithms of the catalytic rate constants and the donor numbers of the solvents:

$$\lg k = -0.577 + 0.0725\,DN \ (r = 0.996), \qquad (4)$$

$$\lg k = -1.91 + 0.106\,DN \ (r = 0.997). \qquad (5)$$

Donor solvents solvate the initial hydrazine, the transition state, and the substrate. The catalytic activities of dimethylformamide, dioxan, and pyridine in reactions of tosylhydrazine and diphenylphosphinic acid hydrazide with phenyl isocyanate and picryl chloride show that the solvation of the substrate does not play a significant role; the different influences of the above solvents are probably a result of the solvation of either the transition state or the initial hydrazine. The approximately same efficiencies of catalysis by donor solvents in reactions of diphenylphosphinic acid hydrazide with phenyl isocyanate and picryl chloride as well as the absence of catalysis in the reactions of *N*-ethyl-*N*-diphenylphosphinylhydrazine and *N*-methyl-*N*-tosylhydrazine[103,197] confirm quite convincingly that solvation involves the hydrogen atom of the imino-group in the initial hydrazide. Consequently the influence of donor solvents in reactions of phenyl isocyanate with phosphorus acid hydrazides and sulphonic acid hydrazides, which leads to an increase of the rate, is most probably associated with the specific solvation of the transition states in these reactions. The effectiveness of the catalysis by donor solvents depends both on the structure of the nucleophile and on the type of substrate employed[197,199].

4. Stabilisation of the Reaction Products

The parallel variation of the thermodynamic stability of the reaction products and the deviations from the reactivity–basicity relation have been demonstrated for the interactions of 4-nitrophenyl acetate with alcohols, peroxides, amines, hydrazines, and hydroxylamines[78]. However, the observed deviations show that this type of correlation is not general, particularly when the reactivities of different atoms are compared. The thermodynamics of the stabilisation of the reaction products is important in the interaction of hydrazine and methoxyamine with the carbonium ion of Malachite Green[79,164]. It has been recognised that factors promoting the stabilisation of the reaction products stabilise also the transition state[8,79,80,200-202].

5. Orbital Splitting

The high reactivity of nucleophiles with a lone electron pair at the α-atom can be explained[4,202] in terms of the theories of reactions controlled by the charge and the disposition of the boundary molecular orbitals of the reactants, i.e. the highest occupied orbital (HOMO) and the lowest unoccupied orbital (LUMO). The free energy of the reaction between a nucleophile and a substrate is determined by an equation whose first term describes the electrostatic interaction of the charges of the reactants in the course of the reaction and the second describes the formation of a covalent bond in the transition state[203]. The use of this equation in the study of the interaction of the ClO^- and HO^- ions with the same substrate permitted the conclusion that the former is more nucleophilic despite its lower basicity constant; the theoretical postulates have been confirmed by experimental data[4].

The lone-pair electrons in hydrazine, hydroxylamine, disulphides, and the ClO^- ions are oriented, relative to the electron pair interacting with the electrophile to form a covalent bond, in a manner which leads to the splitting of the orbitals[9,203]. Such splitting can be detected in photoelectron spectra[205,206]. The splitting of the orbitals increases the HOMO orbital energy, which affects the physical properties of the α-nucleophile: the ionisation potential, the redox potential, and the polarisability[9,207,208]. The occupied π^* orbital interacts more strongly with the "electronic" σ^* orbital compared with the unperturbed π orbitals of the usual nucleophiles; there is then a possibility not only of allowed $\pi \rightarrow \pi^*$ transitions but also of transitions of the type $\pi^* \rightarrow \sigma^*$ (Fig. 1). The latter factor is responsible for the increased reactivity[4,209]. The atom adjoining the lone-pair electrons in (XXVI) is more electronegative than the carbon or hydrogen atom in (XXVII), giving rise as a result to a positive inductive effect and reducing thereby the charge on the nucleophilic atom[5,209]. All these factors reduce the extent of the interaction with the approaching substrate:

$$\underset{\text{(XXVI)}}{R{-}\underset{\cdot\cdot}{\ddot{O}}\leftarrow\underset{\cdot\cdot}{\ddot{O}}\!:} \qquad \underset{\text{(XXVII)}}{R{-}CH_2{-}\underset{\cdot\cdot}{\ddot{O}}\!:} \ .$$

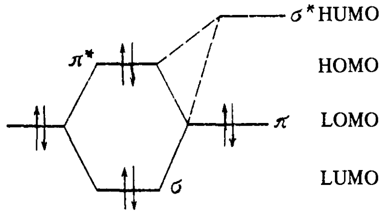


Figure 1. Energy levels of the molecular orbitals of α-nucleophiles: HUMO—highest unoccupied molecular orbital; HOMO—highest occupied molecular orbital; LOMO—lowest occupied molecular orbital; LUMO—lowest unoccupied molecular orbital.

In such cases the change in nucleophilic properties opposes the effect of the change in p*K*; indeed the CH_3COO^- ion is $10^{4.6}$ times more basic than the $CH_3CH_2O^-$ ion[5], while H_2O_2 is 10^4 times stronger as an acid than H_2O.[209]

Comparison of the energy levels of the ClO^- and HO^- ions shows that in the ClO^- ion there is interaction between the p,π orbitals of the oxygen and chlorine atoms, resulting in the splitting of the energy levels (Fig. 2). Because of this, the HUMO level in the ClO^- ion lies far above the corresponding energy level in the HO^- ion[4]. Fig. 2 shows that the ClO^- ion requires a smaller expenditure of energy ($\Delta E_1 > \Delta E_2$) and is therefore more reactive than the HO^- ion. The intermediate thus produced is stabilised by a three-orbital covalent bond and its loosening and dissociation are considerably hindered owing to the absence of an effect by the approaching group. The validity of the above treatment is confirmed by the fact that the α-effect is shown by nucleophiles with partial overlapping of the lone electron pair orbitals[4].

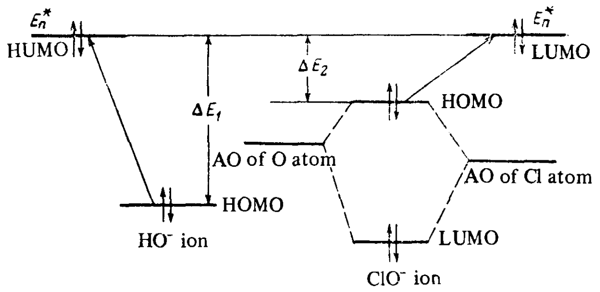


Figure 2. Diagram of the orbital energy levels of the HO^- and ClO^- ions in nucleophilic attack on the *n*th substrate: AO—atomic orbital; E_n^*—energy level of the LUMO of the substrate. The remaining symbols have the same significance as in Fig. 1.

The relation between the proposed explanation of the α-effect and the description of an acid–base type interaction may be analysed within the framework of Edwards' equation[210]:

$$\lg (k/k_0) = \alpha E + \beta H,$$

where α characterises the ability of the substrate to accept electrons and form a covalent bond and β characterises the capacity of the substrate for coordination[4]. For α-nucleophiles, $\alpha > 0$ and $\beta \leqslant 0$, in contrast to ordinary nucleophiles, which do not exhibit an anomalous reactivity (for the latter, $\alpha = 0$ and $\beta \simeq 1$). The ratio α/β then becomes a measure of the factor controlling the reaction: if α/β is large, the reaction is controlled by boundary molecular orbitals; for low values of α/β, the course of the reaction is determined by the charges of the reactants, which should lead to a relation between the α-effect and the redox potentials. If the latter hypothesis is correct, it is to be expected that hydrazine should be oxidised more readily than ammonia, and its redox potential should be higher owing to the higher HUMO energy E^*_n. Experimental data confirm this: the redox potential of hydrazine is higher than that of ammonia[5].

The involvement of an anionic nucleophile in the reaction is accompanied by a decrease of the p,π- p,π electron orbital interaction, because one of these orbitals forms a σ bond. The interaction between p,π and σ orbitals is on the whole less intense than the p,π–p,π interaction; the latter entails an increase of the reactivity of the nucleophile. The foregoing considerations lead to the following conclusion: the positive α-effect is induced by the decrease in the course of the chemical reaction of the overlap integral of the orbitals containing lone-pair electrons; hence one may conclude that the manifestation of the α-effect is determined by the conformation of the α-nucleophile. On this basis, α-nucleophiles can be divided into two groups[5]:

(a) Nucleophiles of the type ROO^-, ClO^-, and RSS^-, which have high p,π orbital repulsion energies in the ground state. Such nucleophiles should exhibit an enhanced reactivity in reactions with both saturated and unsaturated substrates.

(b) The conformation of nucleophiles of the type NH_2NH_2, NH_2OH, and RSSR is such that the p,π–p,π (or sp^3–sp^3) repulsion in the ground state is reduced to a minimum; under these conditions, the orbital splitting is zero.

The conformations of the ground state and the rotational barriers in peroxides[211–213], disulphides[214], F_2O_2,[215] NH_2NH_2,[216,217] NF_2NF_2,[173,218,219] NH_2OH,[174] diarsines[220], and diphosphines[221] have been studied in detail and may be accounted for in terms of a simple rule, described above, concerning the relation between the α-effect and the overlap integral of orbitals with lone-pair electrons. Fig. 3 illustrates examples of these α-nucleophiles in the form of idealised Newman projections[5]. Their molecules should not exhibit the α-effect due to the repulsion of the p,π orbitals; the increase of nucleophilic reactivity noted in certain reactions should be attributed to other causes. For example, the anomalous reactivity of amidoximes in reactions with benzyl bromide is attributed to general intramolecular base catalysis[14].

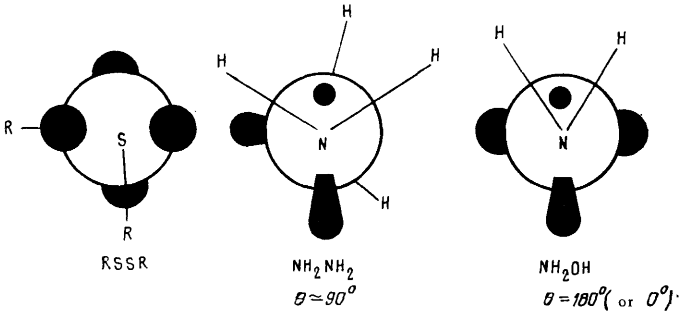
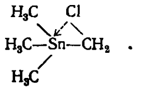


Figure 3. Idealised Newman projections for disulphides RSSR ($\theta = 90°$), hydrazine NH_2NH_2 ($\theta \simeq 90°$), and hydroxylamine NH_2OH ($\theta = 180°$ or $0°$). θ is the torsional angle.

However, one should note that the explanation of the α-effect based on the repulsion of the lone-pair electron orbitals suffers from a significant disadvantage. This is the assumption that the splitting of the energy level necessarily leads to an increase of the HUMO[190]. Quantum-chemical calculations and their thermodynamic analysis have shown, however, that the α-effect for NH_2NH_2 [190,222] and the ClO^- ion[190] cannot be explained solely by taking into account the orbital splitting.

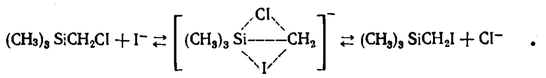
6. Intramolecular Coordination

The anomalous behaviour of "mesoids" (α-carbofunctional compounds of Group IVB elements) is due to the effect of the intramolecular electronic interaction between M and Hal atoms; for example, the effect in chloromethyl(trimethyl)tin (XXVIII) is apparently due to the transfer of the lone-pair electrons of the chlorine atom to the vacant *d* orbital of the Sn atom[223]:



(XXVIII)

However, NQR data for "mesoids" with Ge, Si, and Sn atoms show that, together with the inductive effect of the substituents, there is intramolecular coordination between the atom of the Group IVB element and the halogen. The reactivity of $(CH_3)_3MCH_2Cl$ with respect to nucleophiles increases for different M in the sequence C < Si < Ge < Sn.[131] The latter shows that the site of nucleophilic attack is not only the carbon atom of the CH_2 group but also the M atom of the mesoid. For this reason, the relatively high reactivity of chloromethyl(trimethyl)silane has been explained[132] by the stabilisation of the transition state (XXIX) owing to the simultaneous interaction of the approaching halide ion with the carbon atom and the vacant 3*d* orbitals of the silicon atom:

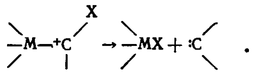


$$(CH_3)_3SiCH_2Cl + I^- \rightleftarrows \left[(CH_3)_3Si\overset{Cl}{\underset{I}{\cdots}}CH_2\right]^- \rightleftarrows (CH_3)_3SiCH_2I + Cl^- \ .$$

(XXIX)

The outgoing Cl^- ion may interact with silicon and carbon atoms; a similar mechanism has been postulated for the reactions of chloromethyl(trimethyl)silane with SCN^- and $C_2H_5O^-$ ions.

The rearrangements involving the cleavage of the M–C bond and the migration of the substituent X from the carbon atom to the M atom constitute fairly convincing evidence for intramolecular coordination between the M and X atoms of mesoids:



$$\rangle M-{}^{+}\overset{X}{C}\langle \ \rightarrow \ \rangle MX + {:}C\langle \ .$$

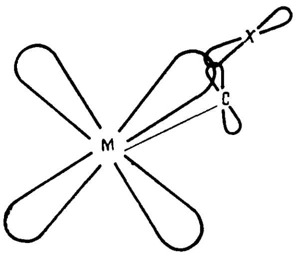


Figure 4. The formation of a three-centre bond of the "closed" type in "mesoids" (α-carbofunctional compounds of Group IVB elements).

The coordination interaction between the M and X atoms takes place with transfer of the σ electrons of the X atoms involved in the C–X bond to the vacant *d* orbitals of the M atom. This leads to the formation of a three-centre bond of the "closed" type[132] (Fig. 4) due to the overlapping of the *p*, σ orbitals of the X atom, the sp^3-hybridised orbitals of the carbon atom, and the vacant *d* orbitals of the M atom. The axes of these orbitals are directed to the interior of a non-equilateral triangle formed by the M, C, and X atoms. The occurrence of intramolecular coordination in mesoids has been questioned[224] in view of the very low coordination capacity of the M atom. The decreasing basicity of amino-derivatives of mesoids is pointed out in support of this view, while the Ge > Sn > Si series corresponds to the generally accepted electronegativity scale of the M atoms[224].

The ^{35}Cl NQR frequencies for alkyl chloromethyl ethers, which are appreciably lower than for alkyl chlorides, are attributed to the interaction between the lone-pair electrons of the oxygen atom and the σ electrons of the C–Cl bond in α-halogeno-ethers[225]. Voronkov[136,226] believes that the most likely explanation of the anomalous properties of the halogen atoms in α-halogeno-ethers is the direct interaction of the oxygen atom with the C–Cl bond and the formation of an intramolecular three-centre bond of the "closed" type (Fig. 5). This bond is formed between the O, C, and Cl atoms with participation of the sp^3-hybridised orbitals of the carbon atom, the *p*, σ orbitals of the chlorine atom, and the lone-pair electrons of the oxygen atom.

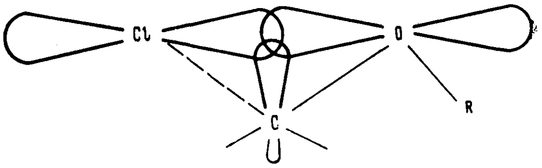


Figure 5. The formation of an intramolecular three-centre bond of the closed type in α-halogeno-ethers.

V. QUANTITATIVE ESTIMATE

Together with the qualitative description of the α-effect, it is of interest to consider the quantitative criteria for the assessment of this phenomenon. The increase of nucleophilic reactivity (i.e. the magnitude of the α-effect) has been estimated in terms of the ratio of the rate constants for reactions of α-nucleophiles and compounds which do not exhibit the α-effect (reference standards) when the basicities of both are the same; the α-effect varies significantly as a function of the type of nucleophiles used as the reference standards[79,164,166]. The latter were usually the HO^- ion, NH_3, glycine, and glycylglycine (Table 5). The α-effects in heteroaromatic compounds have been estimated as the ratios of the rate constants for the reactions of diazines and pyridine bases[32]. The ratios of the rate constants for the reactions of oximate and phenoxide (or alkoxide) ions of the same basicity were adopted as the α-effects in the reactions of 4-nitrophenyl acetate with oximate anions in water[9]. The α-effects in reactions with hydroxamic acids has been estimated as the ratios of the rate constants for the reactions of hydroxamic acids and phenoxide ions derived from phenols having the same p*K* values as the acids[189].

Table 5. Estimation of the α-effects in reactions of nucleophiles with various substrates.

Substrate	$k(HOO^-)^a/k\cdot(HO^-)^b$	$k(NH_2NH_2)^c/k\cdot(HO^-)$	$k(NH_2O^-)^d/k\cdot(HO^-)$	$k(ClO^-)^e/k\cdot(HO^-)$	$k(HOO^-)/k\cdot(CF_3CH_2O^-)^f$	$k(NH_2NH_2)/k\cdot$(glycyl-glycine) g	$k(NH_2NH_2)/k\cdot$(glycine amide) h	$k(NH_2NH_2)/k\cdot(NH_3)$ i
Benzonitrile	66 000^{163}	—	—	—	—	—	—	—
4-Chlorobenzonitrile	22 000^{163}	—	—	—	—	—	—	—
4-Methylbenzonitrile	19 000^{163}	—	—	—	—	—	—	—
3-Bromobenzonitrile	35 000^{163}	—	—	—	—	—	—	—
4-Cyanobenzoic acid	1 180^{161}	—	—	—	—	—	—	—
Bromophenylacetic acid	12.7^{161}	—	—	—	—	—	—	—
α-Bromo-4-toluic acid	13.1^{161}	—	—	—	—	—	—	—
Bromoacetate	3.6^{4}	23.2^{4}	3.6^{4}	—	—	—	—	8^{4}
Ethyl acetate	$10^{-4\;163}$	—	—	—	—	—	—	—
Phenyl acetate	420^{5}	$6.2\cdot10^{-3\;5}$	$9.2\cdot10^{-3\;5}$	—	80^{230}	52^{166}	—	4.65^{232}
4-Methylphenyl acetate	—	—	—	—	—	—	—	2.77^{232}
3-Nitrophenyl acetate	—	—	—	—	—	—	—	7.82^{232}
4-Nitrophenyl acetate	386^{5}	0.8^{5}	0.2^{5}	—	58^{5}	44^{166}	—	12.2^{232}
2,4-Dinitrophenyl acetate	303^{5}	5.5^{5}	0.9^{5}	—	41^{5}	33^{166}	—	—
1-Acetoxy-4-methoxypyridinium perchlorate	246^{5}	0.8^{5}	0.5^{5}	—	51^{5}	17^{166}	—	—
Sarin	46.5^{86}	—	$10^{-3\;86}$	—	0.3^{86}	—	—	—
Diethyl 4-nitrophenyl phosphate	15.5^{181}	—	—	—	—	—	—	—
Tetraethyl pyrophosphate	104^{86}	—	1.2^{86}	—	12.7^{86}	—	—	—
4-Nitrophenyl phosphate	—	126^{94}	40^{94}	—	—	—	3.1^{166}	—
2,4-Dinitrophenyl methyl phosphate	200^{85}	—	1.0^{85}	—	—	—	—	—
Benzyl bromide	34^{14}	—	—	—	—	—	—	—
Methyl iodide	—	12.4^{128}	—	—	—	—	5.0^{166}	12.4^{128}
Methyl tosylate	45.3^{79}	—	—	—	62^{79}	0.97^{9}	—	—
Ethyl tosylate	—	3.0^{4}	—	8.3^{4}	—	—	—	—
4-Nitrophenyl sulphate	125^{161}	—	—	—	—		6.0^{166}	—
Malachite Green	10 810^{79}	50.6^{70}	7.3^{79}	40.5^{79}	—	28^{164}	—	—
1-Fluoro-2,4-dinitrobenzene	45 000^{79}	—	—	—	—	18.3^{164}	19.4^{166}	—
1-Iodo-2,4-dinitrobenzene	—	—	—	—	—	22.7^{164}	21.3^{166}	—
1-Chloro-2,4-dinitrobenzene	78 000^{79}	3.5^{227}	—	—	—	30.8^{164}	35.6^{166}	—
Picryl chloride	—	—	—	—	—	16.8^{164}	23.2^{166}	—
6-Acetoxyquinoline	—	—	—	—	—	38.0^{27}	—	—
8-Acetoxyquinoline	—	—	—	—	—	25.2^{27}	—	—
δ-Thiovalerolactone	—	3.1^{120}	$6\cdot10^{-3\;120}$	—	—	—	—	—
Trifluoroethyl thioloacetate	—	3.2^{228}	0.5^{228}	—	—	—	—	—
Tris(acetylacetonato)silicate(IV) anion	47^{189}	—	—	—	—	—	—	—
Methyl formate	—	—	—	—	—	250^{231}	280^{231}	—
Formaldehyde	166^{130}	—	—	—	—	—	—	—
Acetaldehyde	13^{130}	—	—	—	—	—	—	—
H_3O^+	$10^{-4\;16}$	$10^{-8\;16}$	$10^{-10\;229}$	$10^{-8\;16}$	—	—	—	—
trans-Pt(Py)$_2$Cl$_2$	—	—	—	—	—	—	—	6.3^{137}
$RCOOH \rightleftharpoons RCOO^- + H^+$	0.61^{155}	—	—	—	1.02^{155}			

[a] $pK(HOO^-) = 11.60$. [b] $pK(HO^-) = 15.27$. [c] $pK(NH_2NH_2) = 8.11$. [d] $pK(NH_2O^-) = 6.20$. [e] $pK(ClO^-) = 7.10$. [f] $pK(CF_3CH_2O^-) = 12.36$. [g] pK(glycylglycine) = 8.25. [h] pK(glycine amide) = 8.10. [i] $pK(NH_3) = 9.21$.

One must note that the ratios $k(HOO^-)/k(HO^-)$ and $k(HOO^-)/k(NH_3)$ should be used with much caution as quantitative estimates of the α-effect, because the points on the Brønsted plots for HO^- and NH_3 very frequently lie below the straight line for primary amines and alkoxide ions; this finding apparently has nothing in common with the enhanced nucleophilic properties of the reactants due to the α-effect[71]. This probably explains the appreciable variation of the α-effect in reactions of aryl acetate esters (Table 5) and Malachite Green, for which Dixon and Bruice[79,164] estimated the α-effects as the ratios of the nucleophile/glycine, nucleophile/glycylglycine, and nucleophile/hydroxide ion rate constants.

The relative α-effects in the acylation reactions of hydrazine derivatives may be estimated as the ratios of the rate constants for the reactions of benzoylhydrazine and aniline with the same substrate[233]. Shevchenko[233] showed that the nucleophilic addition reactions (reactions with phenyl isocyanate) are the most sensitive to the α-effect and are followed, in this respect, by nucleophilic substitution at the carbonyl carbon atom (interaction with benzoyl chloride, ethyl chloroformate, phenyl chloroformate, and benzoic and acetic anhydrides). Substitution at an aromatic carbon atom (reactions of picryl chloride) exhibits an extremely insignificant α-effect. From our point of view, the ratio of the rate constants for the reactions of the given α-nucleophile and a primary arylamine of the same basicity must be regarded as a more correct estimate of the α-effect in hydrazine derivatives[104,234]. Table 6 presents quantitative estimates of the α-effect obtained using in certain cases the rate constants calculated by the Brønsted equations for the reactions of arylamines with phenyl chloroformate[234], phenyl isocyanate[234], phenyl thioisocyanate[104], benzoyl chloride[234], and picryl chloride[104]. In terms of the sensitivity to the α-effect, the substrates investigated can be arranged in the following sequence: phenyl isocyanate > benzoyl chloride > phenyl thioisocyanate > phenyl chloroformate > picryl chloride (Table 6). In reactions involving the hydrazides of phosphorus acids, those involving nucleophilic addition also exhibit the greatest α-effect; N-ethyl-substituted derivatives of these compounds show an α-effect smaller by a factor of 5–20 under the same conditions (Table 6).

Many workers have suggested a close relation between the α-effect and the β constant in the Brønsted equation[79,164,166]. A linear correlation has been noted between the magnitude of the α-effect and the β constant[166]. For hydrazine derivatives, correlations of this type are characterised by an appreciable scatter of the points, which can probably be accounted for by the fact that the basicity constants of hydrazine derivatives and the rate constants for the reactions were measured in different media.

The linear correlation between $k(HOO^-)/k(HO^-)$ and the product $\alpha\beta$ of the coefficients of Edwards' equation for reactions employing ethyl acetate, 4-nitrophenyl acetate, 4-nitrophenyl methylphosphonate, 1-chloro-2,4-dinitrobenzene, α-bromo-4-toluic acid, and bromoacetic acid, which was noted by Behrman and coworkers[161], is promising for the quantitative estimation of the α-effect.

Table 6. Estimated α-effects in various reaction series involving hydrazine derivatives[104,123].

Hydrazine derivative	Phenyl chloroformate	Phenyl isocyanate	Picryl chloride	Hydrazine derivative	Phenyl chloroformate	Phenyl isothiocyanate	Picryl isocyanate
$RC_6H_4NHNH_2$	80	235	0	$(C_6H_5)_2PONHNH_2$	2772	331	32
$RC_6H_4N(C_2H_5)NH_2$	0	42	0	$(C_6H_5)_2PON(C_2H_5)NH_2$	565	173	37
$C_6H_5N(Alk)NH_2$	29	95	0	$(C_6H_5O)_2PONHNH_2$	1783	204	8
$RC_6H_4CONHNH_2$*	192	20 000	3	$(C_6H_5O)_2PON(C_2H_5)NH_2$	83	64	7
$RC_6H_4SO_2NHNH_2$	62	—	—	$(C_6H_5O)_2PSNHNH_2$	967	182	10
$AlkCONHNH_2$	—	3 600	—	$(C_6H_5O)_2PSN(C_2H_5)NH_2$	158	110	8

*In reactions with benzoyl chloride, the α-effect amounts to 7600.

Thus the foregoing findings show that a high reactivity (α-effect) is manifested by compounds with one or several lone-pair electrons at an atom adjoining the reaction centre. There are a wide variety of causes responsible for the α-effect, but none of them can fully explain its manifestations. In considering the α-effect in specific systems, one should probably take into account simultaneously a wide variety of factors which could explain this phenomenon.

It is noteworthy that an enormous amount of experimental data associated with the observation of the α-effect has accumulated largely as a result of the application of kinetic methods. Unfortunately there have been almost no studies on the nature of the α-effect by physical methods, and quantum-chemical procedures for calculations on reactions involving α-nucleophiles have also been inadequately used.

Despite the fact that the problem of the α-effect in organic compounds requires further systematic study and development, the relevant available information can already be used in analytical chemistry, in fine chemical organic syntheses on an industrial scale, and in the manufacture of physiologically active preparations and polymeric materials.

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Oxidative Coupling of Aromatic Systems under the Influence of Transition Metal Compounds

I.V.Kozhevnikov and K.I.Matveev

Liquid-phase reactions involving the oxidative coupling of aromatic systems (including heteroaromatic systems and aryl derivatives of the elements) to the corresponding biaryls under the influence of transition metal compounds are examined. Attention is concentrated on reactions under the influence of palladium(II) salts and complexes, which constitute the group of the most important reactions of this class. Oxidative coupling under the influence of other oxidants, including strong one-electron oxidants such as cobalt(III), manganese(III), cerium(IV), iron(III), etc., is considered for comparison. The bibliography includes 124 references.

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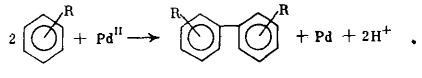
I. INTRODUCTION

Oxidative coupling reactions with formation of a C–C bond have been known for a long time. Interest in them increased considerably after the development of the Wacker process for the oxidation of olefins[1] and particularly in the last ten years in connection with the discovery of the coupling of aromatic compounds to biaryls under the influence of palladium salts[2].



The rapid publication of the relevant patent literature (see, for example, Refs. 3–16) indicates the potential importance of this reaction for the development of a single-stage method of synthesising biaryls, which are valuable intermediates in organic synthesis. Until recently the most universal method for the synthesis of biaryls was the technologically complex two-stage Ullmann reaction[17]. Coupling under the influence of palladium(II) salts proceeds under milder conditions via a non-radical mechanism, which creates conditions for a high selectivity. Furthermore, coupling may be achieved catalytically as a result of the regeneration of palladium(II) by means of oxidants, including O_2.

The early studies on this reaction, published before 1969, have been examined in previous reviews[1,18–20] and have been briefly discussed in other publications[21,22]†. Further research into the oxidative coupling of the aromatic systems, including heteroatomatic systems and aryl derivatives of the elements, greatly extended the applications of the reaction and deepened the understanding of its mechanism. Significant advances have been achieved in the development of oxidative coupling catalysts based on palladium(II). Numerous studies have been published recently on the oxidative coupling of aromatic compounds under the influence of other oxidants, in the first place strong one-electron oxidants such as cobalt(III), manganese(III), cerium(IV), iron(III), etc. These data are extremely useful for the understanding of the mechanism of coupling under the influence of palladium(II). Such problems are in fact the subject of the present review. which covers the literature published up to the middle of 1976. It is noteworthy that, together with the term "oxidative coupling", the terms "oxidative dimerisation", "oxidative dehydrodimerisation", and "oxidative pairing" are used in the literature. The first term is used in the review because in the author's view it is the most accurate and embraces not only symmetrical but also asymmetric coupling reactions. Stern's[18] and Moritani and Fujiwara's[23] reviews may be recommended to those who wish to become acquainted with the related oxidative coupling and olefin arylation reactions under the influence of palladium(II).

II. OXIDATIVE COUPLING UNDER THE INFLUENCE OF PALLADIUM(II) COMPOUNDS

1. AROMATIC (CARBOCYCLIC) COMPOUNDS

In 1965 Van Helden and Verberg[2] reported for the first time the oxidative coupling of aromatic compounds to biaryls under the influence of palladium(II) in acetic acid:

$$2RH + Pd^{II} \rightarrow R{-}R + Pd^0 + 2H^+ .$$

Subsequent studies showed that the composition of the products of the reaction depends on the conditions. The coupling of benzene derivatives has been most fully investigated (see Table). Compounds of the naphthalene series and probably other aromatic condensed systems also enter into this reaction.

Depending on the substrate, when aromatic hydrocarbons are acted upon by $PdCl_2$ + NaOAc in acetic acid, biaryls are formed in yields of 25–81% [here and henceforth the yields are quoted relative to the initial amount of palladium(II)][2]. In the absence of sodium acetate the reaction does not occur. Davidson and Triggs found that, when palladium(II) is used in the form of $Pd(OAc)_2$, products resulting from the acetoxylation of the ring and the

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† During the preparation of this paper for the Press, the following reviews were also published: R. A. Sheldon and J. K. Kochi, Adv. Catalysis, **25**, 274 (1976); I. I. Moiseev, Zhur. Vses. Khim. Obshch. im. Mendeleeva, 22, 30 (1977); H. W. Krause, R. Selke, and H. Pracejus, Z. Chem., **16**, 465 (1976).

side chain are formed together with the coupling products[24,25,27] (for further details about the acetoxylation, see Refs. 22 and 26). Thus biphenyl (66%) and phenyl acetate (16%) were obtained from benzene in acetic acid. Benzyl acetate (40–45%) was the main product from toluene. In the presence of $HClO_4$ in acetic acid the reaction is sharply accelerated and the yield of coupling products increases as a result of the suppression of the acetoxylation reaction[24,27]. The addition of alkali metal acetates also accelerates the overall reaction, but under these conditions there is an increase in the yield of acetoxylation products[24,28]. The acetoxylation of benzene and toluenee by palladium(II) acetate in acetic acid is almostly completely suppressed when the reaction is carried out under oxygen at a pressure of 50 atm.[29] when mainly coupling products are formed. When benzene was allowed to interact with $Pd(OAc)_2$ in benzene solution and with $PdSO_4$ in 20% aqueous sulphuric acid solution, only coupling products were obtained[24,27].

The oxidative coupling of aromatic systems to biaryls under the influence of palladium(II).

Substrate	Oxidant	Medium	*T*, °C	Time, h	Product R-R	Yield, % Pd	Refs.
		Aromatic compounds					
Benzene	$PdCl_2$	HOAc, NaOAc	90	5.5	Biphenyl	71	2
Benzene	$PdSO_4$	H_2O, H_2SO_4	80	24	Biphenyl	54	27
Benzene	Pd $(OAc)_2$	DOAc, $HClO_4$	80	0.5	Biphenyl	44	27
Benzene	Pd $(OAc)_2$	HOAc	100	16	Biphenyl	66	25
Benzene	Pd $(CF_3COO)_2$	CF_3COOH	25	24	Biphenyl	40	32
Benzene	Pd $(NO_3)_2$	HOAc	95		Biphenyl	4,5	31
Benzene	$(C_2H_4PdCl_2)_2$	HOAc, $AgNO_3$	80	20	Biphenyl	99	34
Benzene	(styrene.$PdCl_2)_2$	HOAc, $AgNO_3$	80	20	Biphenyl	68	34
Benzene	$PdCl_2$	HOAc, $AgNO_3$	80	20	Biphenyl	40	34
Benzene	(cyclo-$C_6H_{10}PdCl_2)_2$	HOAc, $AgNO_3$	80	20	Biphenyl Terphenyl	3 9	34
Toluene	$PdCl_2$	HOAc, NaOAc	110	7	Bitolyl (2,3'—25%; 3,3'—20%; 3,4'—35%; 4,4'—20%)	75	2
Toluene	Pd $(OAc)_2$	HOAc, $HClO_4$	50	1.5	Bitolyl (3,4'—34%; 4,4'—42%)	37	27
Toluene	Pd $(OAc)_2$	HOAc, $HClO_4$, Hg $(OAc)_2$	25	30	Bitolyl (3,4'—27%; 4,4'—67%)	95	35
Toluene	$(C_2H_4PdCl_2)_2$	HOAc, $AgNO_3$	80	20	Bitolyl (4,4'—31%)	61	34
Ethylbenzene	Pd $(CF_3COO)_2$	CF_3COOH	25	340	Diethylbiphenyl	53	32
Cumene	$PdCl_2$	HOAc, NaOAc	110	7	Bicumenyl	81	2
Cumene	Pd $(CF_3COO)_2$	CF_3COOH	25	340	Bicumenyl (3,4'—48%; 4,4'—40%)	42	32
Anisole	$PdCl_2$	HOAc, NaOAc	110	7	Dimethoxybiphenyl	60	2
Anisole	Pd $(CF_3COO)_2$	CF_3COOH	25	340	Dimethoxybiphenyl (2,4'—35%; 3,4'—15%; 4,4'—35%)	49	32
Chlorobenzene	$PdCl_2$	HOAc, NaOAc	110	7	Dichlorobiphenyl (3,4'—40%;	56	2
Chlorobenzene	$(C_2H_4PdCl_2)_2$	HOAc, $AgNO_3$	80	20	Dichlorobiphenyl (4,4'—20%)	70	34
Nitrobenzene	Pd $(CF_3COO)_2$	CF_3COOH	70	48	Dinitrobiphenyl (2,3'—48%)	21	32
Nitrobenzene	$(C_2H_4PdCl_2)_2$	HOAc, $AgNO_3$	80	20	3,3'-Dinitrobiphenyl	60	34
Methyl benzoate	$PdCl_2$	HOAc, NaOAc	110	7	Dimethoxycarbonylbiphenyl	42	2
Phenyl pivalate	$PdCl_2$	HOAc, NaOAc	110	7	Dipivaloyloxybiphenyl	25	2
$PhC(Me)_2CH_2C(O)OMe$	$PdCl_2$	HOAc, NaOAc	110	7	Biaryl	45	2
Biphenyl	$PdCl_2$	HOAc, NaOAc	110	7	Quaterphenyl (3,4'—45%; 4,4'–22%)	40	2
o-Xylene	Pd $(OAc)_2$	HOAc, NaOAc	110	10	Bixylyl (3,4,3',4'—65%)	73	2
m-Xylene	$PdCl_2$	HOAc, NaOAc	110	7	Bixylyl	60	2
p-Xylene	Pd $(CF_3COO)_2$	CF_3COOH	25	340	2,5,2',5'-Bixylyl	19	32
p-Xylene	$(C_2H_4PdCl_2)_2$	HOAc. $AgNO_3$	80	20	2,5,2',5'-Bixylyl	38	34
m-Di-isopropylbenzene	$PdCl_2$	HOAc, NaOAc	110	7	3,5,3',5'-Tetraisopropylbiphenyl	25	2
2,6-Di-isopropylphenol	$PdCl_2$	HOAc, NaOAc	100	3	*p,p'*-Diphenoquinone	23	30
2,6-Di-isopropylphenol	$Pd(OAc)_2$	HOAc	100	3	*p,p'*-Diphenoquinone	21	30
2,4-Di-isopropylphenol	$PdCl_2$	HOAc, NaOAc	100	3	*o,o'*-Biphenol	1	30
2,6-Dimethoxyphenol	$PdCl_2$	HOAc, NaOAc	100	3	*p,p'*-Diphenoquinone	25	30
		Heterocyclic compounds					
Furan	Pd $(OAc)_2$	HOAc	50	2	Bifuryl (2,2'—91%)	45	44
Furan	Pd $(OAc)_2$	HOAc, NaOAc	50	2	Bifuryl (2,2'—93%)	80	44
Furan	Pd $(OAc)_2$	DMF	96	3	Bifuryl (2,2'—90%)	98	44
2-Methylfuran	Pd $(OAc)_2$	DMF	98	1	Dimethylbifuryl (2,2'—90%)	48	45
Furfural	Pd $(OAc)_2$	Furfural	97	1	Diformyl-2,2'-bifuryl	62	45
2-Methoxycarbonylfuran	Pd $(OAc)_2$	HOAc	97	3	Dimethoxycarbonylbifuryl (2,2'—65%); 2,3'—35%)	40	45
2-Ethoxycarbonylfuran	Pd $(OAc)_2$	HOAc	97	3	Diethoxycarbonylbifuryl	45	45
Diacetoxyfurfural	Pd $(OAc)_2$	HOAc	97	3	Tetra-acetoxydiformyl-2,2'-bifuryl	36	45
Benzofuran	Pd $(OAc)_2$	C_6H_6—HOAc	80	6	2,2'-Bibenzofuryl	68	50
5-Methylbenzofuran	Pd $(OAc)_2$	C_6H_6—HOAc	80	6	Dimethyl-2,2'-bibenzofuryl	70	50
Thiophen	Pd $(OAc)_2$	HOAc	70	2	Bithienyl (2,2'—30%; 2,3'—65%)	69	46
Thiophen	$PdCl_2$	H_2O	50	2	Bithienyl (2,2'—95%)	21	44
Thiophen	$PdCl_2$	H_2O, Hg $(NO_3)_2$	50	2	Bithienyl (2,2'—96%)	52	44
Thiophen	Pd $(ClO_4)_2$	H_2O, $HClO_4$	69	2	Bithienyl (2,2'—58%; 2,3'—42%)	12	44
Thiophen + furan	Pd $(OAc)_2$	HOAc	35	4	2-(2-Furyl)thiophen 3-(2-Furyl)thiophen Bithienyl Bifuryl	16 4 15 9	44
Pyrrole	Pd $(OAc)_2$	DMF	70	2	2,2'-Bipyrrolyl	1	44

Table (contd.)

Substrate	Oxidant	Medium	T, °C	Time, h	Product R-R	Yield, % Pd	Refs.
Organoelemental compounds							
C_6H_5HgOAc	$Pd(OAc)_2$	HOAc, LiOAc	90	23	Biphenyl	95	35
(p-$CH_3C_6H_4)_2Hg$	$PdCl_2$	HOAc	90	0.01	4,4'-Bitolyl	100	35
p-$CH_3C_6H_4HgOAc$	$PdCl_2$	HOAc, $HClO_4$	25	0.5	Bitolyl (3,4'—35%; 4,4'—60%)	95	35
(Ferrocenyl)HgCl	Li_2PdCl_4	CH_3OH	—	—	Biferrocenyl	—	61
$C_6H_5HgOAc^a$ + benzofuran	Li_2PdCl_4	C_2H_5OH	25	12	2-Phenylbenzofuran	77	50
					Biphenyl	7	
$C_6H_5HgOAc^a$ + 5-methylbenzofuran	Li_2PdCl_4	C_2H_5OH	25	12	5-Methyl-2-phenylbenzofuran	75	50
					Biphenyl	9	
$C_6H_5Tl(OAc)ClO_4$	$PdCl_2$	HOAc, NaOAc	115	5	Biphenyl	49	63
$(C_6H_5)_2TlCl$	$PdCl_2$	HOAc, NaOAc	115	5	Biphenyl	6	63
p-$CH_3C_6H_4Tl(OAc)ClO_4$	$PdCl_2$	HOAc, NaOAc	115	5	4,4'-Bitolyl	69	63
3,4-$(CH_3)_2C_6H_3Tl(OH)ClO_4$	$PdCl_2$	HOAc, NaOAc	115	5	3,4,3',4'-Bixylyl	66	63
p-$CH_3OC_6H_4Tl(OAc)ClO_4$	$PdCl_2$	HOAc, NaOAc	115	5	4,4'-Dimethoxybiphenyl	70	63
$C_6H_5B(OH)_2$	$Pd(OAc)_2$	HOAc, $HClO_4$	60	0.08	Biphenyl	18	27
$C_6H_5B(OH)_2$	Na_2PdCl_4	H_2O, H_2SO_4	80	0.03	Biphenyl	81	27
p-$CH_3C_6H_4B(OH)_2$	$Pd(OAc)_2$	HOAc, $HClO_4$	60	0.08	4,4'-Bitolyl	—	27
$C_6H_5SO_2Na$	Na_2PdCl_4	H_2O	100	8	Biphenyl	35	65
$C_6H_5SO_2Na$	Na_2PdCl_4	H_2O, $HgCl_2$	100	8	Biphenyl	71	65
p-$CH_3C_6H_4SO_2Na$	Na_2PdCl_4	HOAc	115	8	4,4'-Bitolyl	36	65
p-$CH_3C_6H_4SO_2Na$	Na_2PdCl_4	H_2O, $HgCl_2$	100	8	4,4'-Bitolyl	63	65
p-$CH_3C_6H_4SO_2H$	Na_2PdCl_4	H_2O—C_2H_5OH	81	8	4,4'-Bitolyl	27	65
Catalytic reactions. 1. Oxidation by metal salts							
Benzene	$Pd(CF_3COO)_2$, $Cu(OAc)_2$	CF_3COOH	25	100	Biphenyl	110	32
					Terphenyl (o—40%; m—35%; p—25%)	10	
Furan	$Pd(OAc)_2$, $CuCl_2$	DMF	132	6	Bifuryl (2,2'—91%)	9000	45
Furan	$Pd(OAc)_2$, $CuCl_2$	DMF-H_2O	96	3	Bifuryl (2,2'—82%)	520	45
Furfural	$Pd(OAc)_2$, $CuCl_2$	Furfural	120	3	Diformyl-2,2'-bifuryl	1350	45
Thiophen	$Pd(OAc)_2$, $CuCl_2$	HOAc	98	6	Bithienyl (2,2'—80%)	350	44
Thiophen	$PdCl_2$, $FeCl_3$	H_2O	98	2	Bithienyl (2,2'—85%)	530	44
Thiophen	$Pd(ClO_4)_2$, $Fe(ClO_4)_3$	H_2O, $HClO_4$	69	2	Bithienyl (2,3'—81%)	160	44
Thiophen	$PdSO_4$, $Fe_2(SO_4)_3$	H_2O. H_2SO_4	98	2	Bithienyl (2,3'—77%)	170	44
Thiophen + furan	$Pd(OAc)_2$, $CuCl_2$	DMF	96	2	2-(2-Furyl)thiophen	550	44
					3-(2-Furyl)thiophen	110	
					Bithienyl	460	
					Bifuryl	58	
p-$CH_3C_6H_4HgCl$	$PdCl_2$, $CuCl_2$	HOAc	24	17	4,4'-Bitolyl	650	5
p-$(CH_3)_2CHC_6H_4HgCl$	$PdCl_2$, $CuCl_2$	HOAc	24	17	4,4'-Bicumenyl	740	5
m-$NO_2C_6H_4HgCl$	$PdCl_2$, $CuCl_2$	HOAc	24	17	3,3'-Dinitrobiphenyl	810	5
m-$HOOCC_6H_4HgCl$	$PdCl_2$, $CuCl_2$	HOAc	24	17	3,3'-Dicarboxybiphenyl	670	5
p-$CH_3C_6H_4SO_2Na$	Na_2PdCl_4, $CuCl_2$	H_2O, $HgCl_2$	100	8	4,4'-Bitolyl	380	65
$C_6H_5Tl(OAc)ClO_4$	$PdCl_2$	HOAc, NaOAc	115	5	Biphenyl	380	63
Catalytic reactions. 2. Oxidation by oxydation							
Benzene	$Pd(OAc)_2$, O_2 (60 atm)	HOAc, NaOAc	100	8	Biphenyl	160	25
Benzene	$Pd(OAc)_2$	HOAc, NaOAc	150	4	Biphenyl	3100^b	89
Benzene	$Pd(OAc)_2$, O_2 (1 atm)	H_2O—HOAc, $HClO_4$	68	8	Biphenyl	220	87
Benzene	$Pd(ClO_4)_2$	H_2O—HOAc	25	16	Biphenyl	5700^c	87
Benzene	$Pd(ClO_4)_2$	H_2O—HOAc	68	6	Biphenyl	700^c	87
Toluene	$Pd(OAc)_2$, O_2 (100 atm)	HOAc, NaOAc	100	4	Bitolyl	83	25
Toluene	$Pd(OAc)_2$	Toluene	150	16	Bitolyl (3,3'—27%; 3,4'—35%; 4,4'—13%)	20600^b	88
Toluene	$Pd(OAc)_2$	Toluene	150	4	Bitolyl	7400^b	89
Toluene	$Pd(ClO_4)_2$	H_2O—HOAc	68	6	Bitolyl	6400^c	87
Chlorobenzene	$Pd(OAc)_2$	Chlorobenzene	150	4	Dichlorobiphenyl	400^b	89
Chlorobenzene	$Pd(ClO_4)_2$	H_2O—HOAc	68	6	Dichlorobiphenyl	340^c	87
Phenyl acetate	$Pd(OAc)_2$	Phenyl acetate	150	4	Diacetoxybiphenyl	5700^b	89
Methyl benzoate	$Pd(OAc)_2$	Methyl benzoate	150	4	Dimethoxycarbonylbiphenyl	8500^b	89
Nitrobenzene	$Pd(OAc)_2$	Nitrobenzene	150	4	Dinitrobiphenyl	2500^b	89
Fluorobenzene	$Pd(OAc)_2$	Fluorobenzene	150	4	Difluorobiphenyl	2300^b	89
Trifluoromethylbenzene	$Pd(OAc)_2$	Trifluoromethylbenzene	150	4	Biaryl	700^b	89
o-Xylene	$PdCl_2$, O_2 (1 atm)	HOAc, NaOAc	110	10	Bixylyl (3,4,3',4'—72%)	90	2
o-Xylene	$Pd(OAc)_2$	o-Xylene	150	4	Bixylyl	5700^b	89
o-Xylene	$Pd(ClO_4)_2$	H_2O—HOAc	68	6	Bixylyl (3,4,3',4'—65%)	3000^c	87
m-Xylene	$Pd(OAc)_2$	m-Xylene	150	4	Bixylyl	4100^b	89
m-Xylene	$Pd(ClO_4)_2$	H_2O—HOAc	68	6	Bixylyl	870^c	87
p-Xylene	$Pd(OAc)_2$	p-Xylene	150	4	Bixylyl	400^b	89
p-Xylene	$Pd(ClO_4)_2$	H_2O—HOAc	68	6	Bixylyl	3500^c	87
Dimethyl phthalate	$Pd(OAc)_2$	Dimethyl phthalate	150	4	Biaryl	5200^b	89
Naphthalene	$Pd(OAc)_2$, O_2 (1 atm)	HOAc	115	400	Binaphthyl (1,1'—41%; 1,2'—49%)	1600	41
					Oligomers (tetramer—65%)	1500	
Naphthalene	$Pd(OAc)_2$	Naphthalene	150	4	Binaphthyl (1,1'—43%; 1,2'—50%)	4500^b	89
Catalytic reactions. 3. Oxidation by oxygen in the presence of a catalyst							
Benzene	$PdSO_4$	H_2O—HOAc	84	3	Biphenyl	1600^d	99
Toluene	$Pd(OAc)_2$	H_2O—HOAc	70	2	Bitolyl (2,4'—21%; 3,4'—31%; 4,4'—22%)	1800^d	99
Toluene	$Pd(OAc)_2$	H_2O—HOAc, $Hg(OAc)_2$	70	2	Bitolyl (3,4'—36%; 4,4'—36%)	1900^d	99
Toluene	$PdCl_2$, $H_4SiW_{10}V_2O_{40}$, O_2 (1.5 atm)	H_2O—HOAc	84	3	Bitolyl	920	99
Toluene	$Pd(OAc)_2$	sulpholane	70	3	Bitolyl (3,4'—35%; 4,4'—48%)	610^d	99
Chlorobenzene	$Pd(OAc)_2$	H_2O—HOAc	90	—	Dichlorobiphenyl (2,4'—29%; 3,4'—26%; 4,4'—21%)	$—^d$	100
Chlorobenzene	$Pd(OAc)_2$	H_2O—HOAc, $Hg(OAc)_2$	90	—	Dichlorobiphenyl (2,4'—15%; 3,4'—34%; 4,4'—36%)	$—^d$	100

Table (contd.)

Substrate	Oxidant	Medium	T, °C	Time, h	Product R – R	Yield, % Pd	Refs.
o-Xylene	$Pd(OAc)_2$	H_2O—HOAc	50	2,5	Bixylyl (3,4,3′,4′—92%)	1300[d]	99
Durene	$PdSO_4$	H_2O—HOAc	84	4	Biduryl	670[d]	99

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[a] Analogous products were obtained in a yield of 70–80% in the reaction of *p*-tolyl-, *p*-anisyl-, and *m*-nitrophenylmercury(II) acetates.

[b] Reaction carried out in the substrate undergoing oxidation in the presence of acetylacetone under a pressure of 150 atm of a 1 : 1 $O_2 + N_2$ gas mixture.

[c] Reaction carried out in the presence of $Fe(ClO_4)_3$ and $HClO_4$ under O_2 pressure (1 atm).

[d] Reaction carried out in the presence of HPA-2 having the composition $H_5PMo_{10}V_2O_{40}$ under O_2 pressure (1.5 atm).

It has been established[30] that substituted phenols in acetic acid in the presence of $PdCl_2$ and sodium acetate undergo oxidative coupling with formation of a C–C bond. This process yielded biphenols (1%) and products of their subsequent oxidation–biphenoquinones (17–25%). Phenol coupling products involving the formation of a C–O bond, which are frequently produced in other catalytic systems[18], were not detected.

When $PdBr_2$ and PdI_2 are used in acetic acid solution, oxidative coupling of aromatic compounds does not occur[2]. Palladium(II) nitrate interacts with aromatic compounds in acetic acid to form acetoxylation, nitration, and oxidative coupling products[31]. Thus phenyl acetate (39%), nitrobenzene (14%), and biphenyl (4%) were obtained from benzene. The addition of water, $HClO_4$, and iron(III) sulphate increases the yield of the coupling products.

Clark et al.[32] (see also Gol'dshleger et al.[33]) found that, under the influence of palladium(II) trifluoroacetate in trifluoroacetic acid at room temperature, aromatic compounds give rise to coupling products together with a small amount of phenols, which are probably formed on hydrolysis of the corresponding aryl trifluoroacetates during the separation of the reaction mixtures. The mode of coupling depends on the nature of the aromatic substrate. Benzene and its monosubstituted derivatives give rise preferentially or exclusively to biaryls. This is also observed with *o*- and *m*-xylenes and 1,2,3-trimethylbenzene. Apart from biaryls, alkylbenzenes yield diarylmethanes (mesitylene and durene give rise exclusively to diarylmethanes in 60% yield). Arylmethylation is characteristic of strongly acid media. Similarly phenyltolylmethane was obtained in the reaction of toluene with $Pd(OAc)_2$ in acetic acid in the presence of $HClO_4$.[27]

According to Fujiwara et al.[34], the $(olefin.PdCl_2)_2$ complexes cause the effective coupling of aromatic compounds in the presence of added silver(I), mercury(II), and copper(II) salts or oxides. Best results are obtained in the presence of the $(C_2H_4.PdCl_2)_2$–$AgNO_3$ (1 : 1) system. In the absence of the palladium(II) complex, silver(I) nitrate is inactive. Gaseous products (ethylene, nitrogen dioxide, and HCl) are evolved during the reaction. The yield of biphenyl in the coupling of benzene decreases in the following sequence of palladium(II) complexes: $(C_2H_4.PdCl_2)_2 > (styrene.PdCl_2)_2 > PdCl_2 > (cyclo\text{-}C_6H_{10}.PdCl_2)_2$. It is suggested that the role of $AgNO_3$ is cooperation in the substitution of the olefin for RH in the palladium(II) complex. In addition, the nitrate ion is involved in the reaction as an oxidant, which is indicated by the evolution of nitrogen dioxide.

The influence of substituents in the aromatic substrate shows that oxidative coupling under the influence of palladium(II) has the characteristics of electrophilic substitution in the aromatic ring[2]; electron-donating substituents facilitate the reaction, while electron-accepting substituents retard it. Monosubstituted benzene derivatives give rise to all six theoretical biaryl isomers[2,27]. 2,2′-Isomers are usually formed in an insignificant amount, probably owing to steric hindrance. In the reactions involving monoalkylbenzenes the main coupling products are the 3,4′- and 4,4′-isomers of biaryls. *o*-Xylene gives a mixture of the three possible isomers of bixylyl, in which the 3,4,3′,4′-isomer predominates (more than 60%)[2]. The proportions of the biaryl isomers are almost independent of added acids, salts, (for example NaOAc), and complex-forming agents. It has been shown[35] that the addition of mercury(II) salts significantly increases the yield of 4,4′-isomers in the coupling of alkylbenzenes. In this case the reaction proceeds via the intermediate formation of mercury derivatives of the aromatic compounds (see below). The proportions of the isomers depend strongly on temperature. Thus, when toluene is coupled in acetic acid under the influence of $PdCl_2$ + NaOAc at 25°C, 2,4′- and 2,3′-bitolyls are formed preferentially (in yields of 44 and 24% respectively), while at 200°C the main products are the 3,4′- and 4,4′-isomers (35 and 21%)[35].

Steric effects play a significant role in oxidative coupling. This is indicated by the inertness of the $PdCl_2$ + NaOAc system in acetic acid in relation to *p*-di-isopropylbenzene, *p*-di-(t-butyl)benzene, and mesitylene[2]. It is noteworthy that in trifluoroacetic acid polysubstituted benzene derivatives (mesitylene and durene) show the highest reactivity compared with benzene and its monosubstituted derivatives in the arylmethylation reaction and not the coupling reaction[32]; the reaction mechanism is in this case different (see below).

The coupling of benzene in acetic acid in the presence of $PdCl_2$ and NaOAc proceeds in accordance with the kinetic equation[2].

$$v = k[Pd^{II}][C_6H_6] \tag{1}$$

It is remarkable that the rate of reaction v is independent of the sodium acetate concentration, although in the absence of the latter the reaction with $PdCl_2$ does not occur[2]. This is probably because the relevant measurements were made[2] at a fairly high sodium acetate concentration (approximately 1 M) under saturation conditions.

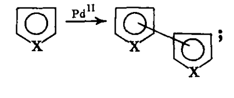
Eqn. (1) is also valid for the coupling of benzene in acetic acid[27] and in aqueous acetic acid[36] in the presence of $Pd(OAc)_2$. The replacement of C_6H_6 by C_6D_6 leads to a marked isotope effect: $k(H)/k(D) = 5.0$.[27] The rate of the reaction in acetic acid falls when water and chloride ions are added[36].

It has been established[27] that, when benzene is coupled in the presence of palladium(II) acetate at 50°C in acetic acid containing 0.5 M $HClO_4$, metallic palladium is not precipitated. The explosive red complex $[Pd(C_6H_6).(H_2O)(ClO_4)]_n$, in which the formal oxidation state of palladium is +1, was isolated instead. The complex decomposes in solution with formation of zero-valent palladium and biphenyl on heating *in vacuo* to 100°C. When chloride ions are added to the solution, palladium(I) disproportionates to bivalent and zero-valent palladium; molecular oxygen, bromine, and $KMnO_4$ oxidise palladium(I) to palladium(II). The role of the palladium(I) complex in the oxidative coupling has not so far been elucidated. The complex probably contains simultaneously bivalent and zero-valent palladium and the latter is stabilised by the benzene molecule. A complex containing palladium in the formal +1 oxidation state and having the composition (quinone).$Pd_2SO_4.3H_2O$ has been isolated in the oxidation of olefins to carbonyl compounds[37]. The zero-valent palladium formed in this reaction is stabilised in solution as a result of the formation of a complex with the olefin, for example $Pd(C_2H_4)_2$. We have suggested the involvement of palladium(I) in the coupling of benzene with ethylene under the influence of $Pd(OAc)_2$.[39]

2. HETEROAROMATIC COMPOUNDS

Like benzene and naphthalene derivatives, aromatic heterocycles undergo oxidative coupling smoothly under the influence of palladium(II). The coupling of five-membered heterocycles of the furan and thiophene series has now been investigated in detail (see Table). Presumably other heteroaromatic systems with various heteroatoms and ring sizes, which do not form inert complexes with palladium(II), would also undergo the coupling reaction. Heteroaryls differ from benzene derivatives by their higher reactivity. The coupling conditions in the heterocyclic series are on the whole analogous to those in the aromatic coupling. Limitations are imposed by the specific properties of the particular classes of heterocyclic compounds. Thus the tendency by furan derivatives to undergo solvolytic ring opening[40] restricts the application of aqueous solvents and rules out the possibility of adding inorganic acids. The coupling of thiophen is less complicated and shows the greatest similarity with the reaction of benzene.

Products of the coupling of five-membered heterocycles were detected when an attempt was made to acetoxylate thiophen[41] and to carbonylate thienyl- and furyl-mercury(II) derivatives[42] under the influence of palladium(II). The oxidative coupling of thiophen and furan derivatives has been studied[43-47]; the reaction proceeds under very mild conditions with formation of a mixture of 2,2'- and 2,3'-biheteroaryls and a small amount of the 3,3'-isomer[44]:



X = O or S.

The coupling of thiophen proceeds in both organic and aqueous solutions, including strongly acid solutions. The yield of bithienyls increases following the addition of mercury(II) salts. The coupling of furan takes place in a wide range of organic solvents[44,45] and in basic aqueous solutions, for example, in H_2O–dimethyl formamide (DMF) mixtures. In acetic acid the yield of biheteroaryls increases after the addition of sodium acetate[44,45]. Thiophen acetoxylation products were not detected under these conditions[41]. The isomeric composition of biheteroaryls depends on the reaction conditions. In acetic acid the ratio of the yields of 2,2'- and 2,3'-bithienyls—the main reaction products—increases after the addition of sodium acetate and water and after the reduction of temperature[44,46]. The ratio of the 2,2'- and 2,3'-isomers of bithienyl increases sharply when aqueous media are used and mercury(II) is added[44].

The reactivity of 2-substituted furan derivatives in the coupling reaction under the influence of $Pd(OAc)_2$ varies as follows in the presence of various substituents: H, CH_3, CHO > $COOCH_3$, $COOC_2H_5$, $CH(OOCCH_3)_2$ > COOH.[45] The sequence was established for electrophilic substitution reactions involving all five-membered aromatic heterocycles[40].

The joint coupling of furan and thiophen makes it possible to obtain in a single stage furylthiophens mixed with bithienyl and bifuryl[44]. The main product is 2-(2'-furyl)-thiophen and a small amount of 3-(2'-furyl)thiophen. It is noteworthy that the synthesis of furylthiophens by other methods is very complex[48,49].

The interaction of benzofuran with $Pd(OAc)_2$ in a benzene–acetic acid mixture yielded 2,2'-bibenzofuryl (68%), 2-phenylbenzofuran (12%), and biphenyl (4%).[50] The ratio of the reaction products indicates a much higher reactivity of benzofuran compared with benzene. A similar result was obtained with 5-methylbenzofuran[50].

Pyrrole chars rapidly on interaction with $Pd(OAc)_2$ in acetic acid, DMF, and heptane[44] and only traces of 2,2'-bipyrrolyl are formed (1%). It may prove useful to protect the pyrrole ring by *N*-alkylation, because *N*-methylpyrrole is smoothly vinylated by olefins under the influence of palladium(II).[51] Pyridine does not undergo the coupling reaction[44], because it forms a very stable complex with palladium(II).[52]

The kinetics of the coupling of heterocycles have been studied in relation to the reaction of thiophen[46]. The coupling of thiophen under the influence of $Pd(OAc)_2$ in acetic acid proceeds in accordance with the equation

$$v = k[Pd^{II}] \cdot [C_4H_4S]/(1 + K[C_4H_4S]), \qquad (2)$$

which differs from Eqn. (1) by the presence of the denominator $1 + K[C_4H_4S]$, which indicates the formation of an intermediate palladium(II) complex of thiophen with a stability constant, $K = 0.2$ litre $mole^{-1}$ at 70°C. In benzene a similar complex is less stable, the difference between the coordination capacities of benzene and thiophen in relation to palladium(II) being manifested. It is suggested[46] that palladium(II) forms a complex with thiophen via the sulphur atom. The kinetic isotope effect in the coupling of [2,5-D_2]thiophen in acetic acid is $k_2(H)/k_2(D) = 1.8$ [k_2 is the rate constant for the attack by palladium(II) on the 2-position in thiophen][46]. In aqueous solution the rate of reaction of thiophen with $PdCl_2$ is given by the equation[47]

$$v = k[Pd^{II}][C_4H_4S]/[H^+]^a \; [\bar{Cl}]^b,$$

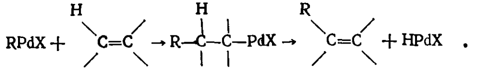
where $a \leqslant 1$ and $2 < b < 3$. A similar kinetic equation holds[1] for the oxidation of olefins by an aqueous solution of $PdCl_2$.

3. ORGANOELEMENTAL COMPOUNDS

The oxidative coupling of aryl derivatives of metals and non-metals [for example, mercury(II), thallium(II), boron(III), etc.] to biaryls under the influence of palladium(II) is discussed in this section. The coupling of organoelemental compounds takes place as a rule very readily and, in contrast to the coupling of hydrocarbons, makes it possible to obtain a unique biaryl isomer and not a mixture of isomers, the structure of the isomer depending on the organoelemental compound (see Table). These reactions proceed via the mechanism involving the substitution of the element by palladium(II), [18,19] which has been well established in the chemistry of palladium, and for this reason are of fundamental importance for the understanding of the mechanism of aromatic coupling under the influence of palladium(II).

Heck was the first to show[53, 60] the considerable preparative possibilities of such reactions in relation to the arylation of olefin and acetylene derivatives. Mercury(II) compounds proved to be the most effective. Tin(IV), lead(IV), etc. compounds have also been used. It is suggested[53-60] that the short-lived intermediate RPdX plays a decisive role in the reaction:

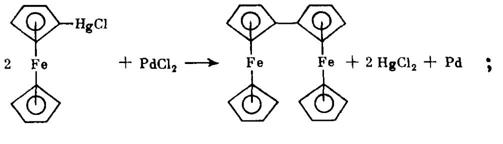
$$\mathrm{RHgX + PdX_2 \rightarrow RPdX + HgX_2} \quad ,$$

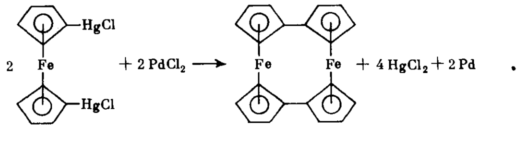


In the absence of unsaturated compounds RPdX gives rise to oxidative coupling products:

$$\mathrm{2RPdX \rightarrow R{-}R + PdX_2 + Pd} \quad .$$

Oxidative coupling of RHgX derivatives (R = phenyl, *p*-tolyl, *p*-cumenyl, *m*-nitrophenyl, *m*-carboxyphenyl, etc.) takes place at 25°C with high yields of the corresponding biphenyl derivatives[5]. A new C–C bond is then formed almost exclusively at the site of the initial addition of mercury(II). The coupling of (*p*-tolyl)HgOAc in acetic acid under the influence of $(\mathrm{PdOAc})_2$ is fairly slow, but is sharply accelerated by the addition of $\mathrm{HClO_4}$; $(p\text{-tolyl})_2\mathrm{Hg}$ reacts instantaneously also in the absence of $\mathrm{HClO_4}$.[35] Heterocyclic mercury(II) derivatives react analogously[42]. The reaction with ferrocene gave a high yield of biferrocenyl[61, 62]:





Arylthallium(III) derivatives react with $\mathrm{PdCl_2}$ in acetic acid in the presence of sodium acetate to form biaryls [Eqn. (3)][63]. As in the coupling of mercury(II) derivatives, the C–C bond is formed at the site of the initial addition of thallium(III); a small amount of side products comprising hydrocarbons RH and RCl is formed. The reaction proceeds with substitution of thallium(III) by palladium(II) in RTl(III).[63] Here $\mathrm{PdCl_2}$ is active also in the absence of NaOAc, but the addition of the latter accelerates the reaction. The inorganic products of the reaction are zero-valent palladium and thallium(I). Thallium(III), formed by reaction (3), probably oxidises metallic palladium to palladium(II), which makes the reaction catalytic in relation to palladium(II):

$$\begin{gathered}\mathrm{2RTl\,(III) + Pd\,(II) \rightarrow R{-}R + Pd + 2Tl\,(III)}\ , \\ \mathrm{Tl\,(III) + Pd \rightarrow Tl\,(I) + Pd\,(II)}\ . \end{gathered} \tag{3}$$

On reaction with palladium(II) salts, Grignard reagents give rise to coupling products with intermediate substitution of magnesium(II) by palladium(II):[64]

$$\begin{gathered}\mathrm{C_6H_5MgX + PdX_2 \rightarrow C_6H_5PdX + MgX_2}\ ; \\ \mathrm{2C_6H_5PdX \rightarrow (C_6H_5)_2 + PdX_2 + Pd}\ . \end{gathered}$$

A similar reaction takes place smoothly with aromatic and heterocyclic compounds also under the influence of copper(II), silver(I), iron(III), cobalt(II), nickel(II), ruthenium(IV), rhodium(III), etc. salts; iridium, osmium, and platinum compounds are less active[64].

The coupling of organic derivatives of non-metals (boron and sulphur) also involves the substitution of these elements by palladium(II). Benzene- and 3-methylbenzeneboronic acids give rise to biphenyl and 4,4′-bitolyl respectively after interacting for several minutes with $\mathrm{Pd(OAc)_2}$ in acetic acid in the presence of $\mathrm{HClO_4}$:[27]

$$\mathrm{2C_6H_5B\,(OH)_2 + Pd\,(II) + H_2O \rightarrow (C_6H_5)_2 + 2B\,(OH)_3 + Pd + 2H^+}\ .$$

Arenesulphinic acids and their salts are converted into biaryls in the presence of palladium(II) with liberation of $\mathrm{SO_2}$ [Eqn. (4)][65]. The reaction takes place in aqueous and organic media and the addition of mercury(II) salts catalyses the coupling reaction. Similar reactions may also be expected for aryl derivatives of silicon, because phenylation of olefins by trimethylphenylsilane in the presence of palladium(II) is known[66]. For the same reason, there is probably also a possibility of aromatic coupling via a stage involving the substitution of phosphorus in triphenylphosphine and of antimony in triphenylstibine for palladium(II), since the above compounds are capable of arylating styrene with a high yield [Eqn. (5)][23]:

$$\mathrm{2\,(}p\mathrm{\text{-}CH_3C_6H_4)\,SO_2Na + Pd\,(II) \rightarrow 4,4'\text{-}(C_6H_4CH_3)_2 + Pd + 2SO_2 + 2Na^+}\ ; \tag{4}$$

$$\mathrm{(C_6H_5)_3P + CH_2{=}CHC_6H_5 \xrightarrow{Pd(OAc)_2}}\ trans\text{-}\ \mathrm{C_6H_5CH{=}CHC_6H_5}\ . \tag{5}$$

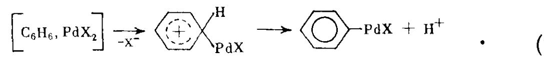
4. THE OXIDATIVE COUPLING MECHANISM

The oxidative coupling of aromatic, heteroaromatic, and organoelemental compounds under the influence of palladium(II) includes a slow stage in which the aromatic ring undergoes electrophilic substitution and proceeds via the intermediate formation of σ-arylpalladium(II).[18,19] This is preceded by the rapid formation of an intermediate arene–palladium(II) complex in accordance with Eqn. (6); this complex has been detected by kinetic methods in the thiophen coupling reaction[46]:

$$\mathrm{C_6H_6 + PdX_2 \rightleftarrows [C_6H_6,\ PdX_2]}\ . \tag{6}$$

The involvement of a σ-arylpalladium(II) is confirmed by the following data: (1) the acceleration of the reaction by electron-donating substituents and its inhibition by electron-accepting substituents: (2) the formation of coupling products when organoelemental compounds containing an aryl–element σ bond interact with palladium(II); (3) the marked kinetic isotope effect in the coupling of $\mathrm{C_6D_6}$ and [2,5-$\mathrm{D_2}$]thiophen; (4) the first order of the reaction with respect to palladium(II) and the substrate; (5) the acceleration of the coupling by the addition of alkali metal acetates, which promotes the abstraction of H^+; (6) other data.

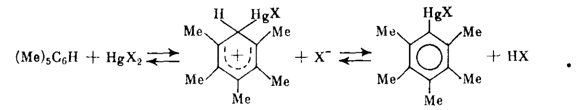
It is usually believed[67] that electrophilic substitution in the aromatic ring proceeds via mechanism(7) in two stages with formation of a cyclohexadienyl intermediate. The marked kinetic isotope effect in the oxidative coupling shows that the rate-limiting stage in reaction (7) is the abstraction of a proton from the cyclohexadienyl intermediate[27,46]:



(7)

Similar behaviour has been observed in the mercuration of aromatic compounds[67]. According to Yatsimirskii et al.[36], the anion bound to palladium(II) cooperaties in the abstraction of H^+ in reaction (7). The absence of deuterobenzene when the coupling is carried out in D_2O and DOAc shows that reaction (7) is irreversible[27]. Reaction (7) does not involve hydride transfer, because 2,2′-bibenzofuryl, obtained on coupling [2-D]benzofuran, does not contain dueterium[50].

The cyclohexadienyl intermediate in reaction (7) is an analogue of stable arenonium ions formed as intermediates in many reactions involving the electrophilic substitution of a hydrogen atom in an aromatic ring[68-70]. Nitration and halogenation of aromatic compounds, alkylation of aromatic compounds by olefins in the presence of Lewis acids, and the numerous reactions involving the migration of substituents in the aromatic molecule and their intermolecular transfer, investigated by Koptyug and coworkers[71], belong to this group of reactions. Reaction (7), involving the formation of a σ-arylpalladium(II), is analogous to the familiar reactions of arenonium ions[71], for example:



Here the cyclohexadienyl intermediate was detected by ultraviolet and ^1H NMR spectroscopy[72].

The subsequent fate of the σ-arylpalladium(II) (RPdX) is less definite. Van Helden and Verberg[2] rule out a radical decomposition of RPdX, because in an oxygen atmosphere phenol is absent from the reaction products; futhermore, the reaction is not affected by inhibitors of free radicals. The formation of coupling products at the instant of the liberation of zero-valent palladium from diarylpalladium(II) (RPdR) [Eqn. (9)] appears to be most likely:

$$RPdX + RPdX \rightarrow RPdR + PdX_2\ , \qquad (8)$$

$$RPdR \rightarrow R{-}R + Pd\ . \qquad (9)$$

This hypothesis is based on the exceptional ease of formation of coupling products from diarylmercury(II) derivatives under the influence of palladium(II).[35] The synthesis and reactions of σ-aryl derivatives of nickel(II), palladium(II), and platinum(II) of the type $RM(C_6H_4F)(PEt_3)_2$, where R = Ph or Me, constitutes a direct model of reaction (9).[73] The above nickel(II) and palladium(II) compounds decompose in solution with formation of coupling products and the zero-valent metal:

$$RPd(C_6H_4F)(PEt_3)_2 \rightarrow R{-}C_6H_4F + Pd + 2PEt_3\ .$$

The complex $NiBr(C_6H_5)(PEt_3)_2$ decomposes rapidly in toluene at 80°C with a quantitative yield of biphenyl; it has been suggested[73] that the reaction proceeds via a disproportionation stage:

$$2NiBr(C_6H_5)(PEt_3)_2 \rightleftarrows Ni(C_6H_5)_2(PEt_3)_2 + NiBr_2(PEt_3)_2\ , \qquad (10)$$

$$Ni(C_6H_5)_2(PET_3)_2 \rightarrow (C_6H_5)_2 + Ni(PEt_3)_2\ . \qquad (11)$$

The pathway leading to the formation of RPdR from RPdX has not been elucidated; we believe that it involves the disproportionation stage (8), similar to reaction (10). It has been suggested in a number of studies[22,32] that the substrate molecule is attacked by RPdX in accordance with the equation

$$RPdX + RH \rightarrow RPdR + HX\ . \qquad (12)$$

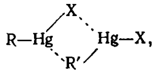
Reaction (12) does not conflict with data on the influence of the ring substituent and on isotope effects, but it is inconsistent with kinetic data. Since the electrophilic activity of RPdX must be lower than that of PdX_2, reaction (12) cannot be faster then reaction (7). One should therefore expect that stage (12) becomes rate-limiting and that the overall oxidative coupling process is of second order with respect to RH. This is inconsistent with experiment and necessitates the abandonment of the hypothesis of stage (12). Reaction (8) must be fast despite the low concentration of RPdX in the reaction mixture. There is no direct experimental confirmation of this, but numerous data for exchange reactions involving organometallic derivatives of beryllium, magnesium, cadmium, mercury, lead, zinc, and other metals have shown that reactions of type (8) are frequently very fast (for further details, see Reutov et al.[74]). In view of the profound analogy between the reactions of mercury(II) and palladium(II) with unsaturated compounds[19,74], the results for mercury(II) compounds are the most instructive. The kinetics and mechanisms of the exchange reactions of alkyl and aryl derivatives of mercury(II) have been studied in detail; the available data[74] show that such reactions proceed fairly readily, which may be an indication of the involvement of stage (8) in oxidative coupling.

Thus the principal features of the mechanisms of the oxidative coupling of aromatic compounds under the influence of palladium(II) can be represented by the sequence of reactions (6)–(9), among which reactions (7) and (8) determine the isomeric composition of the coupling products. It is possible to calculate the ratio of the rate constants for attack by palladium(II) on various positions in the substrate and to find the statistical proportions of the isomeric biaryls [i.e. the proportions obtained when the probabilities of reactions (8) are the same for different RPdX isomers]. By comparing the statistical and experimental proportions of the isomers, it is possible to obtain information about the rate of the exchange reaction (8) for different RPdX isomers. Fine polar effects of the group R in reaction (8) can be discovered in this way.

As an example, we shall consider the coupling of thiophen. When this reaction is carried out in acetic acid under the influence of $Pd(OAc)_2$ at 70°C with $[C_4H_4S]$ = 2.0 M, the experimental ratios of the 2,2′-, 2,3′-, and 3,3′-bithienyls are 6.4 : 13.8 : 1 (Kozhevnikov et al.[46]), while the statistical ratios are 3.2 : 3.6 : 1. Thus reaction (8), which leads to the asymmetric 2,3′-isomer, is much faster than the analogous reactions giving rise to the symmetrical 2,2′- and 3,3′-isomers. The concerted influence of the 2-thienyl and 3-thienyl groups, which have different electropolar properties, is probably manifested here. This effect is known for the "symmetrisation" reactions of RHgX:[74]

$$RHgX + R'HgX \rightarrow RHgR' + HgX_2\ . \qquad (13)$$

It has been established that reaction (13), involving the formation of asymmetric mercury derivatives, is faster than the fastest of the reactions where the symmetrical derivatives R_2Hg and R'_2Hg are formed from RHgX and R′HgX. This synergistic effect indicates the occurrence of reaction (13) [and in the case which we are considering also of reaction (8)] via the cyclic transition state



which corresponds to the S_Ei mechanism[74]. The preferential formation of asymmetric bithienyls in the reaction of thiophen with $Pd(OAc)_2$ may serve as confirmation of the occurrence of reaction (8) in oxidative coupling. More reliable conclusions require a broad analysis, for which the available data are as yet insufficient.

The mechanism discussed above refers to oxidative coupling in non-acid and moderately acid media. Coupling in strongly acid media (trifluoroacetic acid[32], acetic acid with added $HClO_4$ [27]) may proceed via a different mechanism. When alkylbenzenes are coupled in strongly acid media, diarylmethanes are formed together with biaryls. Under these conditions, polyalkylbenzenes (mesitylene, durene) yield mainly diarylmethanes[32]. Analogous products are formed when very strong oxidants [cobalt(III), cerium(IV), manganese(III), etc.)] act on alkylbenzenes. In this case coupling proceeds via a radical mechanism involving a stage in which an electron is transferred from RH to the oxidant (see Section III). In view of the similarity of the coupling products, a radical mechanism cannot be ruled out also in the case of coupling under the influence of palladium(II) in strongly acid media, particularly for reactions of polyalkylbenzenes. It is noteworthy that even thallium(III), which usually reacts with aromatic compounds via an electrophilic substitution mechanism, is capable of abstracting an electron from RH in trifluoroacetic acid with formation of a radical-cation[75] (Section III).

5. CATALYTIC REACTIONS

Catalytic oxidative coupling reactions are of greatest practical interest. For these to occur, palladium(II) must be regenerated from zero-valent palladium under the influence of an oxidant. The oxidants employed are O_2, copper(II), iron(III), vanadium(V), heteropolycompounds, etc. The most suitable industrial oxidant is oxygen; other oxidants may be used in laboratory practice, for example, the salts of metals in the highest oxidation states, hydrogen peroxide, or organic peroxides. Coupling under the influence of molecular oxygen, catalysed by palladium(II), can be divided into processes of two types: (1) those in which zero-valent palladium is oxidised by molecular oxygen and (2) those in which zero-valent palladium is reversibly oxidised by the effective oxidant, which plays the role of an agent transferring electrons from zero-valent palladium to oxygen‡; these reactions are considered separately below. Examples of catalytic reactions are presented in the Table. In the discussion of the catalytic coupling of aromatic compounds attention has been concentrated on fundamental research and only a selection of the patent literature is covered.

(a) General Discussion

Oxidative coupling under the influence of palladium(II) results in the formation of inactive zero-valent palladium, which is then converted into metallic palladium. In order to achieve the catalytic process, it is therefore necessary to oxidise zero-valent palladium to active palladium(II):

$$2RH + Pd(II) \rightarrow R{-}R + Pd(0) + 2H^+ , \qquad (14)$$

$$Pd(0) + Ox \rightarrow Pd(II) + Red. \qquad (15)$$

Depending on the conditions, any of the reactions (14) and (15) may be the rate-limiting stage of the catalytic process; hence follows the necessity for finding the optimum conditions. This problem was first solved successfully for the liquid-phase oxidation of olefins to carbonyl compounds[76,77] and has been examined in detail for these reactions in a number of reviews[1,18,78]. The principles underlying the selection of catalytic systems for the oxidation of olefins are largely applicable also to oxidative coupling reactions when account is taken of the specific features of the latter.

The choice of oxidants based on the oxidation potential is restricted at the lower limit by the requirement for a fairly high oxidation potential in order to regenerate palladium(II) and at the upper limit by the requirement for chemical inertness with respect to the organic substrate being oxidised. When a reversibly acting oxidant is used, the upper limit to its oxidation potential is set by the potential of molecular oxygen. The quantity $E_0[Pd_{met}/Pd(II)]$—the standard oxidation potential of the $Pd_{met}/Pd(II)$ pair whose values have been measured in various media—is usually employed as a criterion for the selection of oxidants[79]. However, this criterion is not entirely correct, because in real catalytic systems the reduced palladium is not precipitated and remains in solution in the form of zero-valent palladium complexes[78]. Such complexes, having the composition $Pd(olefin)_2$, have been detected in the oxidation reactions of ethylene and propene in aqueous palladium(II) solutions[37]. $E_0[Pd(0)/Pd(II)]$—the potential of the Pd(0)/Pd(II) pair, where Pd(0) does not refer to metallic palladium but to a zero-valent palladium complex in solution—must be regarded as a more accurate criterion[37,78]. The accurate oxidation potential of the Pd(0)/Pd(II) pair is not available, but there is not doubt that this potential is less negative than that of the $Pd_{met}/Pd(II)$ pair. For this reason, oxidants (for example, *p*-benzoquinone in the absence of Cl^- ions[37]) weaker than those which might have been thought suitable on the basis of the value of $E_0[Pd_{met}/Pd(II)]$ are also suitable for the regeneration of palladium(II). Together with the oxidation potential, an important characteristic of the oxidant is its ability to form zero-valent palladium complexes in the catalytic system[37].

The optimum reaction conditions for the given oxidant are usually selected by introducing ligands with definite coordination properties in relation to the Pd^{2+} ion[78]. The standard oxidation potential of the $Pd_{met}/Pd(II)$ pair depends significantly on the ligands present in the reaction system. In the absence of ligands capable of forming stable complexes with the Pd^{2+} ion (for example, in dilute solutions of palladium perchlorate or sulphate), the standard oxidation potential of the electrode process $Pd_{met} = Pd^{2+} + 2e^-$ is very high ($E_0 = 0.987$ V). In the presence of

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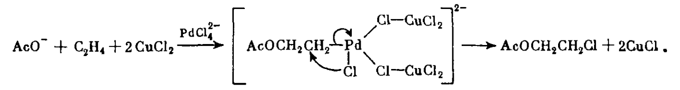
‡ Here and henceforth the term reversibly acting oxidant is understood to imply an oxidant whose oxidised form (Ox) can be rapidly regenerated by treating the reduced form (Red) with molecular oxygen under the reaction conditions.

ligands binding Pd^{2+} into fairly stable complexes (for example, Cl^-, Br^-, CN^-, etc.), the absolute value of the standard oxidation potential of the $Pd_{met}/Pd(II)$ pair diminishes. For example, $E_0 = 0.632$ V for the electrode process $Pd_{met} + 4Cl^- = PdCl_4^{2-} + 2e^-$.[79] Hence it follows that, for the same oxidant, the introduction into the reaction system of ligands forming stable complexes with Pd^{2+} should increase the rate of reaction (15) and reduce that of reaction (14), while exclusion of the ligands from the reaction mixture should lead to the opposite consequences. Since palladium(II) complexes are extremely labile, these thermodynamic predictions are indeed observed in practice.

The use of an oxidant with a higher potential should accelerate reaction (15), which, however, does not always happen owing to kinetic difficulties. An example is provided by molecular oxygen. The standard electrode potential of the process $2H_2O = O_2 + 4H^+ + 4e^-$ is 1.228 V.[79] Consequently direct oxidation of zero-valent palladium by oxygen is thermodynamically feasible in the presence of any ligand. However, in reality this process is very slow and requires severe conditions. The oxidation of zero-valent palladium by oxygen is significantly facilitated in the presence of reversibly acting oxidants, which are capable of effecting rapid electron transfer from zero-valent palladium to oxygen[78]. Copper(II) salts are usually employed as oxidants of this kind. The number of compounds suitable as reversibly acting oxidants in homogeneous catalysis is small. The discovery of the ability of copper salts to function as reversibly acting oxidants in relation to zero-valent palladium made it possible to achieve the catalytic oxidation of olefins to carbonyl compounds and stimulated the development of a whole series of related catalytic oxidation processes, including oxidative coupling reactions[1]. We therefore believe that it is very important to seek new reversibly active oxidants, the application of which will make it possible to extend significantly the scope of homogeneous metal-complex catalysis in partial oxidation reactions.

Before discussing studies on the catalytic oxidative coupling reactions, certain comments must be made concerning the mechanisms of the oxidation of organic compounds by palladium(II) salts in the presence of oxidants. This process was discussed above within the framework of the multistage mechanism (14)–(15) with the intermediate formation of zero-valent palladium. There is no doubt about the possibility of a multistage process, since reactions (14) and (15) may be carried out independently. At the same time it has been suggested that there is a possibility of a concerted mechanism of the oxidation process in which there is no intermediate formation of reduced palladium and electrons are transferred directly from the organic substrate to the oxidant via palladium(II),[37] the Pd^{2+} ion behaving as a bridge under these conditions. There are as yet no reliably established examples of reactions via the concerted mechanism, but many experimental data indicate its feasibility. They include the influence of the oxidant on the composition of the reaction products. Thus at a high $CuCl_2$ concentration in the oxidation of ethylene in water and acetic acid, saturated chloro-derivatives are formed as side products—ethylene chlorohydrin[80] and β-chloroethyl acetate[81] respectively. Since this happens only in the presence of $CuCl_2$, it has been suggested[81] that the reaction proceeds via the heterolytic cleavage of the C–Pd bond with transfer of the ligand:



Saturated β-halogeno-substituted coupling products were obtained similarly in the reaction of phenylmercury(II) with ethylene[82]. It has been shown[83] that in the reaction of benzene, alkylbenzenes, or their mercury derivatives with palladium(II) in the presence of acetate, chloride, etc. anions, the introduction of an oxidant (for example, $K_2Cr_2O_7$) results in substitution in the aromatic ring. In the absence of the oxidant, only oxidative coupling takes place. Thus the concerted mechanism can promote substitution in the aromatic ring or arylmethylation via the formation of R^+ in the heterolysis of RPdX induced by the oxidant. However, the involvement of the oxidant in reaction (9) leads to coupling. Presumably the former is more likely in the case of strong oxidants and the latter in the case of moderately strong oxidants. This problem requires special study.

Conclusions based on the above thermodynamic consideration of the influence of oxidants and ligands are independent of the reaction mechanism. They are valid also for the concerted mechanism. However, in the concerted mechanism the ability of the ligands to form bridge bonds between palladium(II) and the oxidant, at least in the case of cationic oxidants, is important together with the coordination properties of the ligand in relation to the Pd^{2+} ion.

(b) Oxidation by Metal Salts

The possibility of the regeneration of palladium(II) by copper(II) and iron (III) salts was already noted in the first patent of Van Helden et al.[3] Copper(II) salts are effective as oxidants for zero-valent palladium in the coupling reactions of very reactive aromatic systems, such as the thiophen and furan heterocycles and organoelemental compounds. Benzene and its derivatives are much less reactive in relation to coupling reactions under the influence of palladium(II). This is the reason for the limited applicability of copper salts as oxidants for the coupling reactions of these compounds. The Pd(II)/Cu(II) catalytic system is stable only in the presence of high concentrations of ligands forming stable complexes with palladium(II) and (or) copper(I) (these are usually Cl^- ions)[78]. The optimum concentration of Cl^- in the catalytic solution in water is approximately 1 M,[84] while in non-aqueous solutions it is less but still remains high. Under these conditions, the rate of reaction (14) is fairly high only for very reactive aromatic systems. Benzene and the majority of its derivatives are not included among these. The presence of Cl^- ions induces an appreciable side reaction involving the chlorination of organic compounds and intense corrosion of the apparatus, which also restricts the applications of the Pd(II)/Cu(II) system.

In the presence of palladium(II) as the catalyst, $CuCl_2$ effectively oxidises aryl derivatives of mercury(II) [5] and arenesulphinic acids[65] to biaryls in yields up to 800% [here and henceforth the yields are quoted in relation to palladium(II)]. The coupling of benzene in trifluoroacetic acid under the influence of copper(II) acetate is very slow[32].

The palladium(II)-catalysed oxidative coupling of furan, thiophen, and their derivatives under the influence of copper salts proceeds very readily and may be used as a convenient preparative method for the synthesis of the corresponding bifuryl, bithienyl, and furylthiophen derivatives[44,45,47,85]. Copper salts do not have a significant influence on the isomeric composition of the coupling products. The reaction proceeds in both aqueous and organic solvents (DMF, acetic acid, etc.) in yields up to

9000%. The coupling of furfural to 5,5′-diformyl-2,2′-bifuryl takes place smoothly in furfural and the yield and purity of the products increase after the addition of inert adsorbents to the system, for example, of activated charcoal[45].

The use of iron(II) salts as oxidants in palladium(II)-catalysed coupling of thiophen in aqueous solution makes it possible to obtain bithienyl in yields exceeding 700%.[44,47] The isomeric composition of bithienyl depends significantly on the presence of chloride ions in the reaction medium[47]. 2,2′-Bithienyl is formed in chloride systems with a selectivity up to 90%. In the absence of chloride ions in acid sulphate and perchlorate media 2,3-bithienyl is formed with a selectivity of about 90%, while its synthesis by other methods is extremely complex[86]. An increase of the concentrations of H^+ and Fe^{3+} increases the yield of the 2,3′-isomer, but lowers the catalytic activity. The influence of H^+ has been explained[47] by the protonation of thiophen at the sulphur atom, which entails the deactivation of the aromatic system, particularly in the 2-position of the thiophen ring. The analogous influence of the Fe^{3+} ion is probably due to its coordination to the sulphur atom. It may be that the latter favours the coupling of thiophen via the concerted mechanism[47]. The competitive influence of the Cl^- ion on the rates of stages (14) and (15) leads to an extremum in the dependence of the catalytic activity on $[Cl^-]$. In chloride-free systems the addition of mercury(II) salts sharply accelerates the reaction and leads to the exclusive formation of 2,2′-bithienyl[47]. Apart from Fe^{3+}, V_2O_5 is suitable as an oxidant in the coupling of thiophen in aqueous solution[47]. Iron(III) and vanadium(V) salts have been used as oxidants in the coupling of benzene, naphthalene, and their derivatives in sulphuric acid[6].

Palladium(II) may be regenerated also by thallium(III) compounds. This is indicated by the formation of biphenyl (in a yield of approximately 400%) when an excess of $C_6H_5Tl(OAc)ClO_4$ reacts with palladium(II)[63].

(c) Oxidation with Oxygen

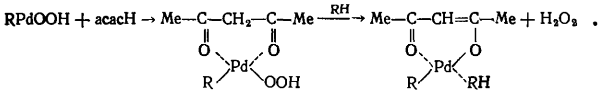
The possibility of the regeneration of palladium(II) by oxygen without cocatalysts was already noted in the first studies[2,29] on the oxidative coupling of aromatic compounds. Davidson and Triggs reported that the coupling of benzene in acetic acid in the presence of $Pd(OAc)_2$ takes place catalytically at an O_2 pressure exceeding 50 atm,[25,29] but the yield of biphenyl under these conditions is low (160% after 8 h at 100°C)[25]. In the presence of $Pd(OAc)_2$ in acetic acid bubbled with O_2 naphthalene gives very slowly (after 400 h) catalytic yields of a mixture of isomeric binaphthyls (1600%) and naphthalene oligomers ranging from the trimer to the hexamer (1500%).[41]

$Pd(ClO_4)_2$ catalyses the coupling of benzene under the influence of oxygen (1 atm) in aqueous acetic acid in the presence of $HClO_4$.[87] The yield of biphenyl increases linearly with time (220% after 8 h at 68°C) and depends on the $HClO_4$ concentration {the yield is a maximum when $[HClO_4] = 2-4$ M}. The activity of palladium(II) depends appreciably on the anion: $Pd(ClO_4)_2$ is twice as active as $Pd(OAc)_2$. The addition of $Fe(ClO_4)_3$ in an amount corresponding to $[Fe^{3+}]/[Pd^{2+}] = 90-200$ has a strong promoting influence. In the presence of Fe^{3+} the yield of biaryls decreases in the sequence toluene > *p*-xylene > *o*-xylene > *m*-xylene > benzene > chlorobenzene. 3,4,3′,4′-Bixylyl is formed preferentially from *o*-xylene, while toluene yields mainly 3,4′-bitolyl. The Fe^{3+} ion behaves as an oxidant in this reaction rather than as a cocatalyst, because there are no data showing the absorption of oxygen and yields of biaryls exceeding 100% (relative to Fe^{3+}) have not been achieved.

The oxidative coupling of benzene and naphthalene derivatives catalysed by palladium(II) carboxylates takes place very effectively in the substrate undergoing oxidation at an elevated temperature and a partial O_2 pressure of about 25 atm. This interesting reaction was discovered by Japanese workers, who investigated it extensively in relation to many aromatic compounds. The influence of conditions on the yield of coupling products[88,89], the relative activities of the aromatic compounds[90], and isotope effects[91] were investigated and the mechanism of the coupling reaction was considered[92,93]. The reaction is usually carried out at 150°C using a 1 : 1 $O_2 + N_2$ mixture in order to exclude the formation of explosive mixtures of organic vapours and oxygen[88]. The yield of coupling products increases with the pressure of the gas mixture up to 50 atm and then ceases to depend on the pressure[89]. The catalytic activity of palladium(II) decreases with increase of the $Pd(OAc)_2$ concentration, although the absolute yield of biaryls increases under these conditions[91]. The yield rises when β-diketones (acetylacetone is best) and EDTA are added to the reaction mixture. The addition of polar solvents, inorganic acids, alkali metal acetates and ligands such as triphenylphosphine, bipyridyl, pyridine, chloride ions, dienes, etc. reduces significantly the yield of oxidative coupling products[89]. The catalyst exhibits a high activity for a long time. Thus, in the coupling of toluene in the presence of $Pd(OAc)_2$ and acetylacetone the yield of bitolyl was 20 600% after 16 h.[88] The influence of the substituent in the benzene ring on the yield of biaryls is typical of electrophilic substitution in the aromatic ring: toluene > *o*-xylene > *m*-xylene > *p*-xylene > mesitylene[89]. The reaction mechanism is not yet entirely clear. A scheme has been proposed for the catalytic process in which oxygen both regenerates palladium(II) and abstracts a hydrogen atom from the molecule of the aromatic compound[92,93]:

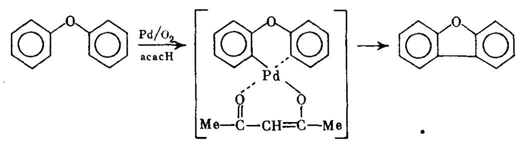
$$\begin{gathered}\mathrm{Pd(OAc)_2 + 2RH \rightarrow RPdR + 2HOAc}\ ,\\ \mathrm{RPdR \rightarrow R{-}R + Pd}\ ,\\ \mathrm{Pd + O_2 + RH \rightarrow RPdOOH}\ ,\\ \mathrm{RPdOOH + acacH \rightarrow RPd{-}acac + H_2O_2}\ ,\\ \mathrm{RPd{-}acac + RH \rightarrow RPdR + acacH}\ .\end{gathered} \tag{16}$$

It is suggested that acetylacetone (acacH) promotes the reaction by forming a stable *cis*-diarylpalladium(II) complex, which then readily gives rise to coupling products[92]:



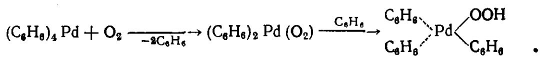
$$\mathrm{RPdOOH + acacH \rightarrow Me{-}C(=O){-}CH_2{-}C(=O){-}Me \xrightarrow{RH} Me{-}C(=O){-}CH{=}C(O){-}Me + H_2O_2}\ .$$

It is of interest that diphenyl ether undergoes an intramolecular coupling reaction, which has been explained[92] by the possibility of the formation, in the first place, of an energetically favourable transition state with a six-π-electron system:



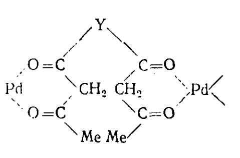
The favourable initial orientation, in one plane, of the benzene rings of the diphenyl ether (owing to conjugation via the oxygen atom) is apparently also important.

It has been suggested that this reaction may resemble the oxidation of triphenylphosphine and alkyl isocyanides by oxygen, which proceeds via zero-valent palladium complexes of molecular oxygen[94]. In this connection it has been postulated[91] that reaction (16) proceeds via a zero-valent palladium complex of O_2:

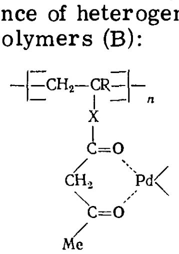


The involvement of free radicals in the reaction is probably ruled out because the coupling reaction is unaffected by inhibitors of free radicals[92].

There are data in the patent literature[8-15] concerning the possible practical achievement of the oxidative coupling of aromatic hydrocarbons at elevated temperatures and under O_2 pressure. The problem of separating the catalyst from the involatile oxidative coupling product is most complex when such processes are employed. In this connection mention should be made of the very important patent of Krause and Doebler[16] for the synthesis of biphenyl derivatives in the presence of heterogeneous palladium catalysts of type (A) or polymers (B):



(A)



(B)

where Y = alkylene, arylene, etc., R = alkyl or aryl, and X = arylene of a single bond. These catalysts are in essence palladium(II) complexes of diketones fixed on the solid surface. The catalysts are chemically equivalent to the homogeneous catalysts based on $Pd(OAc)_2$ and acetylacetone, which were discussed above; this is manifested by the similarity of the conditions in the corresponding reaction. The fundamental difference is the heterogeneous nature of the catalysts, which makes it possible to separate them readily from the reaction products and return them to the cycle.

Methods for attaching metal-complex catalysts to the surface of a solid carrier have been widely developed recently[95] and are extremely promising for the improvement of the technology of oxidative coupling processes. This applies particularly to the coupling reactions discussed in this section, which take place in the substrate undergoing oxidation, in the absence of polar solvents which significantly complicate the use of fixed metal complexes.

(d) Oxidation by Oxygen in the Presence of the Cocatalyst

Direct oxidation of zero-valent palladium by oxygen requires fairly severe conditions. The process may be significantly facilitated by the introduction of a cocatalyst—a reversibly acting oxidant, capable of effecting rapid electron transfer from zero-valent palladium to O_2. The use of classical reversibly acting oxidants-copper(II) salts—in oxidative coupling reactions is limited for reasons partly indicated above. Furthermore, there exist kinetic limitations, which hinder the formation of copper salts: in aqueous solutions the oxidation of copper(I) by oxygen is very rapid, but in organic media, where oxidative coupling is usually carried out, this reaction is very slow owing to the low solubility of CuCl.[96]

Matveev and coworkers suggested that heteropolyacids (HPA) be used as new reversibly acting oxidants, suitable for employment in palladium(II)-catalysed liquid-phase oxidations of olefins[97,98], oxidative coupling of aromatic compounds[99,100], etc. It has been established[99] that many molybdenum and tungsten HPA, which have a sufficiently high potential for the oxidation of zero-valent palladium to palladium(II), can be used for this purpose, including HPA with phosphorus, silicon, arsenic, boron, etc. heteroatoms. However, the most effective compounds of this series are those in which molybdenum or tungsten are partially substituted by vanadium, for example, compounds of the type $H_{3+n}PMo_{12-n}V_nO_{40}$ (henceforth designated by HPA-*n*, $n = 1$–8). Vanadium-containing HPA-*n* have the properties of reversibly acting oxidants and therefore permit the use of molecular oxygen as the oxidant in coupling reactions. The corresponding process may be represented by Eqns. (17)–(19), in which $H_2(HPA)$ is the reduced form of HPA:[99,100]

$$2RH + Pd(II) \rightarrow R{-}R + Pd + 2H^+ \ , \tag{17}$$

$$Pd + HPA + 2H^+ \rightarrow Pd(II) + H_2(HPA) \ , \tag{18}$$

$$\frac{H_2(HPA) + 1/2O_2 \rightarrow HPA + H_2O \quad ,}{2RH + 1/2O_2 \rightarrow R{-}R + H_2O \quad .} \tag{19}$$

It is noteworthy that reaction (19) in organic solvents proceeds faster than the corresponding reaction of copper(I) owing to the higher solubility of $H_2(HPA)$ compared with CuCl.

HPA are of great interest as components of catalysts for oxidative coupling and other partial oxidation reactions. This is due to the comparatively simple methods for their synthesis, ready solubility in both aqueous and organic solvents, and the possibility of varying over a wide range their compositions and hence their oxidation-reduction properties. The latter possibility is at the present time just beginning to be investigated. It is very significant that, in contrast to copper salts, HPA are capable of oxidising palladium in the absence of chloride ions. This makes it possible to achieve a much higher activity of palladium(II) and to eliminate the side reaction involving the chlorination of aromatic compounds, which takes place in the presence of chloride ions. There are reviews[101,102] and a special monograph[103] on the methods of synthesis and properties of HPA. The oxidation-reduction properties of HPA have not as yet been widely discussed in connection with their employment in catalysis. Matveev and coworkers investigated the spectra[104], thermodynamics[105], and kinetics[106] of oxidation-reduction reactions of the HPA-*n*. However, a detailed discussion of these studies is outside the framework of the present review.

The yields of the products of the oxidative coupling of benzene derivatives under the influence of oxygen, catalysed by the Pd(II)/HPA-2 oxidation-reduction system, have been widely studied[99,100]. The reaction proceeds in aqueous acetic acid under an O_2 pressure of 1.5 atm. The yield of biaryls relative to absorbed O_2 in the coupling of benzene, toluene, *o*-xylene, and durene (characterised by the selectivity of the reaction) reaches 70–93%.[99] The yield calculated relative to palladium(II) exceeds 4400% in a single catalytic cycle. The catalytic coupling of aromatic compounds in the presence of HPA-2 as well as the corresponding stoichiometric reaction have the characteristic features of electrophilic substitution in the aromatic ring. The alkylbenzene activity series benzene < toluene and *o*-xylene > durene, determined by the polar and steric influences of the substituents, are consistent with the results of earlier studies on the stoichiometric reaction, Neither HPA-2 nor oxygen affect the composition of the coupling products. As in the stoichiometric reaction, mercury(II) has a marked influence on the proportions of the biaryl isomers. For monosubstituted benzenes, the addition of mercury(II) increases the yield of the 4,4′- and 3,4′-isomers. Thus in the coupling of toluene the yield of 4,4′-bitolyl increases from 22 to 41% with increase of the concentration of $Hg(OAc)_2$ from zero to 0.1 M. In the coupling of *o*-xylene the yield of the 3,4,3′,4′-isomer increases in the presence of mercury(II). It is interesting that the replacement of acetic acid as a solvent by sulpholane has a similar effect on the proportions of the isomeric biaryls[99].

The kinetic data obtained for the coupling of benzene derivatives in the presence of HPA-2 [100] are also consistent with the interpretation of this reaction as electrophilic aromatic substitution: electropositive substituents [OCH_3, $N(CH_3)_2$, OC_6H_5, alkyl] accelerate the reaction, while electronegative substituents (Cl, COOH, CF_3) inhibit it. The influence of chain length (toluene–ethylbenzene > isopropylbenzene > propylbenzene) and of the number of substituents (*o*-xylene > 1,2,4-trimethylbenzene > mesitylene > durene) on the reaction rate corresponds to the usually observed steric influence in electrophilic substitution reactions involving the aromatic ring. The rate of coupling increases after the addition of mercury(II) and reaches saturation at an $Hg(OAc)_2$ concentration of 0.1 M. The orders of the reaction with respect to O_2 and HPA-2 are close to unity, while the order with respect to palladium(II) is less than unity (more precisely 0.4–0.6). These data show that the rate-limiting stage of the oxidative coupling of aromatic compounds under the influence of oxygen, catalysed by Pd(II)/HPA-2, is reaction (19), involving the oxidation of $H_2(HPA)$ to HPA by oxygen[100].

It is very significant that coupling in the presence of HPA proceeds under very mild conditions: at 50–90°C and an O_2 pressure of 1.5 atm. This is an advantage of this process over the palladium(II)-catalysed oxidative coupling in the absence of a reversible oxidant, which takes place at an oxygen partial pressure of about 25 atm.

III. COUPLING UNDER THE INFLUENCE OF OTHER METALS

Apart from palladium(II) compounds, the compounds of many other metals, usually in high oxidation states, may be used for the coupling of aromatic systems. The preparative importance of the coupling reaction involving compounds of these metals is small. Depending on the nature of the metal and the oxidation state, which determines its oxidising properties, coupling may occur via two mechanisms: by electrophilic substitution in the aromatic ring, like the majority of the reactions in the presence of palladium(II), or via electron transfer from RH to the oxidant with formation of a radical-cation. The mechanism of oxidative coupling depends also on the nature of RH, the acidity of the medium, and other factors. The ability of the oxidant to form aryl derivatives is an essential but not sufficient condition for the reaction via the electrophilic substitution mechanism. An increase of the oxidation potential of the oxidant and of the acidity of the medium as well as a decrease of the ionisation potential of RH favour the reaction via the electron transfer mechanism with formation of a radical-cation.

1. COUPLING VIA THE ELECTROPHILIC SUBSTITUTION MECHANISM

The mechanism of these reactions has been little studied, so that only preliminary conclusions may be reached. More complete information is available about coupling under the influence of platinum(II) and platinum(IV): these reactions are very similar to coupling under the influence of palladium(II). Platinum(II) acetate interacts with benzene in an excess of the latter and with benzeneboronic acid in HOAc to form biphenyl[27]. Toluene reacts with $Pt(OAc)_2$ in acetic acid in the presence of $HClO_4$ to form phenyltolylmethane[27]. Chloroplatinic acid is active in the coupling of furan to bifuryl[45] and also readily induces the coupling of toluene in acetic acid in the presence of $Hg(OAc)_2$ and $HClO_4$ to form mainly 4,4′-bitolyl[35]. The degree of reduction of platinum(IV) depends on the $HClO_4$ concentration. In a weakly acid medium platinum(IV) is reduced to platinum(II), while in a strongly acid medium it is reduced to zero-valent platinum[35]. In the last case two moles of biaryl are formed per mole of platinum(IV). It is suggested[35] that the addition of $HClO_4$ increases the electrophilic acitivity of platinum(II) [$PtCl_2$ (Ed. of Translation)] owing to the formation of $Pt(ClO_4)_2$ [which may be more dissociated (Ed. of Translation)]. The coupling of benzene under the influence of H_2PtCl_6 proceeds with a low selectivity in relation to biphenyl in water and aqueous acetic acid[107]; the main product is chlorobenzene. Platinum(IV) is reduced under these conditions to platinum(II) and the reaction proceeds autocatalytically, since platinum(II) catalyses the coupling reaction with participation of platinum(IV).[107] A mechanism has been proposed for the coupling of benzene with the intermediate formation of σ-phenylplatinum(II).[107] The occurrence of aromatic coupling in the presence of platinum(II) via the electrophilic substitution mechanism is also indicated by the well known ability of platinum(II) to catalyse the H–D exchange involving aromatic compounds[107].

Very little is known about coupling under the influence of compounds of other noble metals and data on the mechanisms of these reactions are altogether lacking. Gold(III) sulphate causes slow coupling of benzene in aqueous sulphuric acid, while treatment of toluene with Au_2O_3 in acetic acid in the presence of $HClO_4$ results in the formation of bitolyl[27]. When benzene is coupled under the influence of gold(III) in D_2O, the deuteration is not observed, as in the case of palladium(II)[27]. Ruthenium(IV) and ruthenium(III) compounds are relatively ineffective in the coupling of benzene[30] and furan[45].

As already mentioned, copper, silver, iron, cobalt, nickel, ruthenium, rhodium, iridium, osmium, and platinum as well as palladium(II) compounds interact with Grignard reagents to form coupling products[64]. Recently biaryls were obtained in a high yield from a Grignard reagent under the influence of thallium(I)[108]. The course of the reaction may be represented by the equations

$$RMgBr + TlBr \rightarrow RTl + MgBr_2 \ ,$$

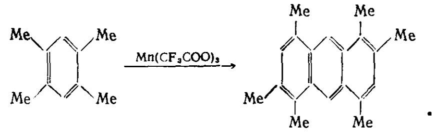
$$2RTl \rightarrow R{-}R + 2Tl \ .$$

However, the formation of a small amount of arylthallium(III) derivatives and aryl bromides indicates a more complex reaction mechanism.

2. COUPLING VIA THE ELECTRON TRANSFER MECHANISM

This class of reactions includes primarily coupling under the influence of strong one-electron oxidants in strongly acid media. These reactions have been studied in detail and their radical mechanism has been demonstrated quite reliably in many instances.

Cobalt(III), manganese(III), and cerium(IV) trifluoroacetates oxidise aromatic hydrocarbons RH in trifluoroacetic acid at room temperature with formation of a mixture of biaryls, diarylmethanes, and aryl trifluoroacetates[109,110]. The composition of the products depends on the nature of RH and the [RH]:[Me] ratio. For the ratio [RH]:[Co(III)] = 0.5, benzene gives a quantitative yield of phenyl trifluoroacetate[109]; in the presence of an excess of benzene, biphenyl was found among the products. However, its yield is insignificant, because biphenyl itself is oxidised by cobalt(III) much faster than benzene[109]. Benzene reacts similarly with cerium(IV)[111]. Toluene and *p*-xylene give rise to benzyl trifluoroacetates, diarylmethanes, and higher oligomers; anisole yields mainly 4,4′-dimethoxybiphenyl (30%). The oxidation of mesitylene results in the preferential formation of bimesityl together with diarylmethane. Durene yields diarylmethane and only traces of a biaryl. When durene was treated with cobalt(III) or manganese(II) trifluoroacetates, hexamethylanthracene was obtained in addition to biarylmethane[110]:



Under these conditions, naphthalene gives a low yield of 1,1′-binaphthyl[110]. The reactions of cobalt(III), manganese(III) and cerium(IV) with aromatic hydrocarbons exhibit considerable qualitative similarities despite certain quantitative differences between the reactivities and product ratios[110].

The heterogeneous oxidation of polymethylbenzenes by iron(III) chloride in non-polar media takes place similarly to oxidation by cobalt, manganese, and cerium compounds[112,113]. In this case chloro-derivatives of the aromatic compounds and polymers are formed together with biaryls and diarylmethanes. Alkylbenzenes react similarly with $SbCl_5$.[114]

It is of interest that the reactions of aromatic perfluorocarbonium ions in $SbCl_5$ solution also lead to coupling products—perfluoropolyaryls. For example, perfluoro-1,3,5-triphenylbenzene was obtained by the reaction between perfluorohexadiene and pentafluorobenzene (80%)[115].

The reactions of aromatic compounds with strong oxidants exhibit a low selectivity in relation to coupling and give many products, as a result of which they are not usually of synthetic value. However, certain reactions can be of preparative importance. For example, the coupling of naphthalene with mesitylene in the presence of $FeCl_3$ makes it possible to isolate 1-(2,4,6-trimethylphenyl)naphthalene in 35% yield[113].

It can be regarded as established that the reactions of aromatic compounds with strong one-electron oxidants proceed via a radical mechanism involving a slow stage in which an electron is transferred from RH to the oxidant[109–113]. This is indicated by the following data. The reactivity of RH increases in the sequence benzene < toluene < *p*-xylene < mesitylene < durene. The ionisation potential of RH diminishes in the same sequence. The above reactions are fully analogous to the electrochemical oxidation of RH, which takes place via electron transfer. The oxidation of benzene and toluene by cobalt(III) trifluoroacetate is of first order with respect to RH and cobalt(III) and there is no kinetic isotope effect. Finally aromatic radical-cations were detected directly by EPR in the reaction of RH and cobalt(III)[109,116]. The reaction mechanism may be represented by the following equations[109–113]:

$$Me^{n+} + RH \rightleftarrows [RH, Me^{n+}] \rightleftarrows [RH^{\dot{+}}, Me^{(n-1)+}] \rightarrow RH^{\dot{+}} + Me^{(n-1)+} ,$$

$$RH^{\dot{+}} + RH \rightarrow [HR\text{—}RH]^{\dot{+}} \xrightarrow[-e,\ 2H^+]{Me^{n+}} \text{biaryl},$$

$$RH^{\dot{+}} \xrightarrow[-H^+]{} R^{\cdot} \xrightarrow[-e]{Me^{n+}} R^+ ,$$

$$R^+ + RH \rightarrow [R\text{—}RH]^+ \xrightarrow[-H^+]{} \text{diarylmethane},$$

$$R^+ + CF_3COOH \rightarrow ROOCCF_3 + H^+ .$$

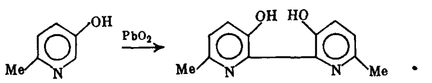
Electron transfer takes place in the molecular complex $[RH.Me^{n+}]$, the decomposition of which yields the $RH^{\dot{+}}$ radical-cation, Subsequently $RH^{\dot{+}}$ may attack the RH molecule with formation of the coupling products or it may lose a proton and an electron under the influence of the base and Me^{n+} may be converted into the carbonium ion R^+. The latter gives rise to substitution and arylmethylation products.

Depending on the conditions, the two-electron oxidants thallium(III) and lead(IV) may react with aromatic compounds via electrophilic substitution in the aromatic ring or via a radical mechanism involving electron transfer[110].

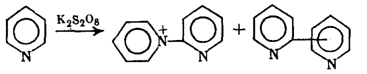
Benzene and toluene are coupled to biaryls under the influence of thallium(III) in aqueous $HClO_4$ and in acetic acid, the reaction being slow and having a low yield[117,118]. The addition of palladium(II) increases sharply the yield of biaryls as a result of the substitution of thallium(III) by palladium(II) in aryl derivatives of thallium(III)[117]. It is well known that thallium(III) usually reacts with aromatic compounds via the electrophilic substitution mechanism[119]. Numerous arylthallium derivatives have been isolated and characterised satisfactorily. However, Elson and Kochi reported[75] that they succeeded in detecting by EPR the durene and 4,4′-bitolyl radical-cations under the conditions of the substitution of thallium in durene and toluene by thallium(III) trifluoroacetate. This demonstrated the possibility of reactions of thallium(III) via a radical mechanism involving electron transfer from RH to thallium(III).

Lead(IV) readily oxidises aromatic compounds to biaryls, diarylmethanes, and aryl ethers with formation of aryllead(IV) derivatives as side products[120,121]; the composition of the product depends on the reaction conditions. In trichloroacetic acid lead(IV) gives products resulting from the metallation of RH, for example *p*-methoxyphenyl-lead(IV) was obtained from anisole in 50% yield[120]. Under more severe conditions (in trifluoroacetic acid), the reaction of lead(IV) with methylbenzenes proceeds via a radical mechanism[121], similar to that of the reactions with one-electron oxidants examined above. These data for thallium(III) and lead(IV) show that even the well-established ability of the metal ion to form aryl derivatives may prove to be an inadequate criterion for the selection of the reaction mechanism. One must also take into account the acidity of the medium and the nature of the ligands and the substrate. In this connection, Nyberg and Wistrand suggested[110] that in media more acid than trifluoroacetic acid reactions with aromatic compounds via electron transfer are not ruled out even in the case of mercury(II).

The coupling reactions of heterocyclic compounds of the pyridine series can be carried out under the influence of strong radical oxidants. Substituted 3-pyridinols react with PbO_2 in benzene solutions to give 2,2′-bipyridyl derivatives, which are remarkable because of their fluoroescence in the visible region under the influence of ultraviolet radiation[122]:



Pyridine is oxidised by potassium persulphate in aqueous solution with formation of the pyridylpyridinium cation and a mixture of bipyridyl isomers[123]:



The ratio of the reaction products depends on the pH of the medium; in acid media the pyridylpyridinium cation is formed preferentially (90%), while in alkaline media the product is 40% of bipyridyl. The addition of silver(I) in an alkaline medium increases the yield of bipyridyl. The radical mechanism of this reaction has been reliably established by detecting the pyridinium radical-cation using EPR.

The oxidative coupling of aromatic systems has a fairly broad universality. The coupling takes place in series of aromatic, heterocyclic, and organoelemental compounds in the presence of a large range of oxidants. Naturally, with such wide variation of the conditions, the reaction mechanism does not remain the same. Having arranged the oxidants effecting the coupling reaction in order of decreasing oxidation potentials, it is possible to observe quite clearly a continuous change in this series from the radical coupling mechanism (via electron transfer with intermediate formation of an aromatic radical-cation) to electrophilic substitution in the aromatic ring and participation of an organometallic intermediate. The selectivity of the conversion of the substrate into the coupling products increases in the same sequence. Oxidative coupling under the influence of palladium(II) salts and complexes is the most important reaction among those in the above class. This is associated with its high selectivity and the possibility of its being catalytic. The latter is a decisive advantage of palladium(II) over other oxidants.

The synthetic possibilities of the reactions are fairly extensive for a wide range of aromatic systems. Among these, the coupling of benzene and its derivatives has been studied in greatest detail. The coupling of benzene to form biphenyl has no significant advantages over the non-catalytic vapour-phase pyrolysis of benzene. However, the coupling of benzene derivatives is really promising as an effective method for the preparation of the corresponding polyfunctional biphenyl derivatives, which are of interest as monomers for polycondensation[124], the synthesis of plasticisers, etc. Oxidative coupling of heterocyclic compounds, where this reaction makes it possible to obtain readily biheteroaryls whose synthesis by other methods is extremely difficult, is extremely promising. The useful properties of biheteroaryls have as yet been inadequately elucidated owing to the difficulty of their synthesis.

The most complex problem, constituting an obstacle to the practical utilisation of catalytic oxidative coupling, is the separation of the catalyst from involatile coupling products. This is a specific disadvantage of homogeneous catalytic processes. The development of metal-complex catalysts deposited on the surface of a solid carrier can probably become the most promising trend in the solution of this problem.

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Topological Principles of the Analysis of Binary Statistical Copolymerisation

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The criteria for the estimation of the characteristics of binary statistical copolymerisation, namely composition, curves for distribution with respect to composition, chemical structure of macromolecules, and parameters of the quantitative estimate of inhomogeneity with respect to composition, are examined on the basis of the most general model of such a process. It is suggested that all copolymeric systems be divided into four classes: (1) classical; (2) classical subject to certain boundary conditions; (3) "unusual" systems of the first kind; (4) "unusual" systems of the second kind ("anomalous" systems). The principles described are illustrated by the analysis of a number of specific models (heterophase copolymerisation, copolymerisation of ionogenic monomers in ionising media, copolymerisation of partly complexed monomers, copolymerisation complicated by reactions involving chain transfer to macromolecules or by depolymerisation reactions, etc.). The bibliography includes 136 references.

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I. INTRODUCTION

A specific alteration of the properties of the final products can be achieved in many instances by replacing homopolymers by copolymers, and the correct choice of the modifying units in the copolymer macromolecules makes it possible to alter in the required direction the rheological, thermomechanical, and physicochemical parameters of materials[1,2]. For many multicomponent systems, an appreciable effect is achieved by the introduction of small amounts of a second monomer, but the contribution of the second component to the resulting property can be by no means always predicted *a priori* and even less so calculated on the assumption of additivity[3]. According to modern ideas, the principal properties of materials (such as thermal stability, chemical stability, tensile strength, residual deformation, modulus of elasticity, radiation stability, and ageing parameters) are determined by the main component of the copolymer, while other properties, for example, surface and volume conductivity, colourability, vulcanisability, surface hardness, adhesion, and ion-exchange capacity, are determined to a significant extent by the nature of the modifying component. Furthermore, the most important parameters of materials based on copolymers are not determined only by the chemical nature of the monomeric units, the average molecular weight, and the average composition, depending no less on the method of introduction of the second component (block, graft, or static copolymers), the chemical structure of the macromolecules, and the characteristics of the distributions with respect to composition and molecular weight[4].

The continuously increasing number of studies devoted to different aspects of copolymerisation (the current bibliography includes more than 100 000 items) faces investigators with the necessity for devising a general classification of the relevant processes. Such classification would promote a more rigorous and well-founded approach to the selection of a realistic detailed copolymerisation model as well as a method and apparatus for the investigation. The employment of such a classification is extremely desirable also for the systematic arrangement and compilation of the existing copolymerisation data. The principal requirements in creating this type of classification may be formulated as follows: firstly, it must be based on the most general copolymerisation model; secondly, the criteria for the estimates must take into account the main specific characteristics of the process; thirdly, the use of the classification should promote the development of a specific experimental programme.

This review deals only with problems concerning binary statistical copolymerisation. Our aim was not to write an exhaustive survey of literature (one of the reasons being the availability of systematic reviews of different branches of copolymerisation[1,4-9]) and we confined ourselves to examining studies where copolymerisation was analysed without the *a priori* assumption of the applicability of the Mayo–Lewis scheme. One should note particularly that the easiest and most widely used method for the interpretation of experimental data employing the average composition of the copolymer increment as the "key" parameter is insufficiently sensitive and reliable to draw final influences about the characteristics of the copolymerisation process. On the other hand, analysis of the complete distribution curves with respect to composition makes it possible to infer much more reliably the process characteristics, particularly when a specific copolymerisation is assigned to classical or "unusual" systems[4,10].

In a series of studies by the present authors the current problems in the statistical theory of copolymerisation are critically analysed. Having examined mainly the "anomalies" of binary copolymerisation, we showed that the classical Mayo–Lewis theory and the widely used schemes which follow from it, for example, the Alfrey–Price scheme, are exceptions to the rule rather than the rule itself. This third and concluding review, constitutes an attempt at a classification of binary copolymerisation processes in terms of topological features, with the principles of kinetic and statistical analyses which follow from it. Naturally, we do not in any way suggest that this is a final classification, but we hope that it will assist investigators working in the field of copolymerisation in developing analytical schemes which are more flexible and realistic than the "classical" schemes mentioned above.

II. FUNDAMENTAL PRINCIPLES OF THE CLASSIFICATION OF BINARY STATISTICAL COPOLYMERISATION PROCESSES

The statistical theory of copolymerisation can be justifiably treated as an independent branch of physical chemistry for three reasons.

(1) The synthesis of copolymers result in the formation of macromolecules with a predetermined configuration; in the general case the composition of the macromolecules depends not only on the composition of the initial monomer mixture but also on the degree of conversion Ψ and the nature of the reaction medium[11].

(2) The principal characteristics of the synthesis of copolymers cannot be described within the framework of the general relations of homopolymerisation processes[1, 12-14].

(3) The properties of copolymers and compositions based on them are in most cases related in a complex manner to the characteristics of the *ensemble* of macromolecules (particularly to the composition[15] and the distribution functions with respect to composition[7,16]) and, in order to obtain even estimates of the corresponding parameters, it is necessary to know at least the mechanism of such copolymerisation.

It is already clear from the foregoing that the technique for the investigation of copolymeric systems must itself be to a large extent specialised and must differ significantly from that for the investigation of homopolymers. Since the most important differences between copolymers and homopolymers are associated with the presence in the macromolecules of fragment of the second monomer (on the nature of the components and their proportions depend also other more complex characteristics of the *ensemble* of the copolymer macromolecules, such as molecular polymorphism, the nature of selective interactions at the intra- and inter-molecular levels, etc.), we selected the composition, the distribution functions with respect to composition, and the stereochemical configuration of the macromolecules as the fundamental criterial parameters in the development of a general classification for the analysis of binary statistical copolymerisation.

We shall examine, for example, a general scheme for the synthesis of macromolecules of statistical copolymers, which includes, as usual, three stages—initiation (I), propagation (II), and termination of kinetic chains (III):

$$\left.\begin{array}{r}\theta \xrightarrow{k_{\mathrm{i}}} q^{*}\ ,\\ q^{*}+\mathrm{A} \xrightarrow{k_{\mathrm{iA}}} q\,\mathrm{A}^{*},\\ q^{*}+\mathrm{B} \xrightarrow{k_{\mathrm{iB}}} q\,\mathrm{B}^{*},\end{array}\right\} \qquad (\mathrm{I})$$

$$\left.\begin{array}{r}
q\mathrm{A}^{*}+\mathrm{A} \underset{k'_{1\mathrm{AA}}}{\overset{k_{1\mathrm{AA}}}{\rightleftarrows}} q\mathrm{AA}^{*}\ ,\\
q\mathrm{A}^{*}+\mathrm{B} \underset{k'_{1\mathrm{AB}}}{\overset{k_{1\mathrm{AB}}}{\rightleftarrows}} q\mathrm{AB}^{*}\ ,\\
q\mathrm{B}^{*}+\mathrm{A} \underset{k'_{1\mathrm{BA}}}{\overset{k_{1\mathrm{BA}}}{\rightleftarrows}} q\mathrm{BA}^{*}\ ,\\
q\mathrm{B}^{*}+\mathrm{B} \underset{k'_{1\mathrm{BB}}}{\overset{k_{1\mathrm{BB}}}{\rightleftarrows}} q\mathrm{BB}^{*}\ ,\\
\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\\
q\,\mathrm{A}_{n_1}\mathrm{B}_{n_2}\mathrm{AA}^{*}+\mathrm{A} \underset{k'_{n\mathrm{AAA}}}{\overset{k_{n\mathrm{AAA}}}{\rightleftarrows}} q\,\mathrm{A}_{n_1+1}\mathrm{B}_{n_2}\mathrm{AA}^{*}\ ,\\
q\,\mathrm{A}_{n_1}\mathrm{B}_{n_2}\mathrm{AA}^{*}+\mathrm{B} \underset{k'_{n\mathrm{AAB}}}{\overset{k_{n\mathrm{AAB}}}{\rightleftarrows}} q\,\mathrm{A}_{n_1}\mathrm{B}_{n_2+1}\mathrm{AB}^{*}\ ,\\
q\,\mathrm{A}_{n_1}\mathrm{B}_{n_2}\mathrm{BA}^{*}+\mathrm{A} \underset{k'_{n\mathrm{BAA}}}{\overset{k_{n\mathrm{BAA}}}{\rightleftarrows}} q\,\mathrm{A}_{n_1}\mathrm{B}_{n_2+1}\mathrm{AA}^{*},\\
q\,\mathrm{A}_{n_1}\mathrm{B}_{n_2}\mathrm{BA}^{*}+\mathrm{B} \underset{k'_{n\mathrm{BAB}}}{\overset{k_{n\mathrm{BAB}}}{\rightleftarrows}} q\,\mathrm{A}_{n_1}\mathrm{B}_{n_2+1}\mathrm{AB}^{*},\\
q\,\mathrm{A}_{n_1}\mathrm{B}_{n_2}\mathrm{BB}^{*}+\mathrm{A} \underset{k'_{n\mathrm{BBA}}}{\overset{k_{n\mathrm{BBA}}}{\rightleftarrows}} q\,\mathrm{A}_{n_1}\mathrm{B}_{n_2+1}\mathrm{BA}^{*},\\
q\,\mathrm{A}_{n_1}\mathrm{B}_{n_2}\mathrm{AB}^{*}+\mathrm{A} \underset{k'_{n\mathrm{ABA}}}{\overset{k_{n\mathrm{ABA}}}{\rightleftarrows}} q\,\mathrm{A}_{n_1+1}\mathrm{B}_{n_2}\mathrm{BA}^{*},\\
q\,\mathrm{A}_{n_1}\mathrm{B}_{n_2}\mathrm{BB}^{*}+\mathrm{B} \underset{k'_{n\mathrm{BBB}}}{\overset{k_{n\mathrm{BBB}}}{\rightleftarrows}} q\,\mathrm{A}_{n_1}\mathrm{B}_{n_2+1}\mathrm{BB}^{*},\\
q\,\mathrm{A}_{n_1}\mathrm{B}_{n_2}\mathrm{AB}^{*}+\mathrm{B} \underset{k'_{n\mathrm{ABB}}}{\overset{k_{n\mathrm{ABB}}}{\rightleftarrows}} q\,\mathrm{A}_{n_1+1}\mathrm{B}_{n_2}\mathrm{BB}^{*},
\end{array}\right\} \qquad (\mathrm{II})$$

$$\left.\begin{array}{r}
q\,\mathrm{A}_{p_1}\mathrm{B}_{p_2}\mathrm{A}^{*}+\lambda \xrightarrow{k_{\mathrm{t}}(1)} \mathrm{L}(1)\ ,\\
q\,\mathrm{A}_{p_1}\mathrm{B}_{p_2}\mathrm{B}^{*}+\lambda \xrightarrow{k_{\mathrm{t}}(2)} \mathrm{L}(2)\ ,\\
q\,\mathrm{A}_{p_1}\mathrm{B}_{p_2}\mathrm{A}^{*}+q\,A_{m_1}\mathrm{B}_{m_2}\mathrm{A}^{*} \xrightarrow{k_{\mathrm{t}}(3)} \mathrm{L}(3)\ ,\\
q\,\mathrm{A}_{p_1}\mathrm{B}_{p_2}\mathrm{A}^{*}+q\,\mathrm{A}_{m_1}\mathrm{B}_{m_2}\mathrm{B}^{*} \xrightarrow{k_{\mathrm{t}}(4)} \mathrm{L}(4)\ ,\\
q\,\mathrm{A}_{p_1}\mathrm{B}_{p_2}\mathrm{B}^{*}+q\,\mathrm{A}_{m_1}\mathrm{B}_{m_2}\mathrm{B}^{*} \xrightarrow{k_{\mathrm{t}}(5)} \mathrm{L}(5)\ ,\\
q\,\mathrm{A}_{p_1}\mathrm{B}_{p_2}\mathrm{B}^{*}+q\,\mathrm{A}_{m_1}\mathrm{B}_{n_2}\mathrm{A}^{*} \xrightarrow{k_{\mathrm{t}}(6)} \mathrm{L}(6)\ .\\
q\,\mathrm{A}_{p_1}\mathrm{B}_{p_2}\mathrm{A}^{*}+\mathrm{A}_{n_1}\mathrm{B}_{n_2} \xrightarrow{k_{\mathrm{t}}(7)} (\mathrm{A}_{n_1}\mathrm{B}_{n_2})^{*}+q\,\mathrm{A}_{p_1}\mathrm{B}_{p_2}\ ,\\
q\,\mathrm{A}_{p_1}\mathrm{B}_{p_2}\mathrm{B}^{*}+\mathrm{A}_{n_1}\mathrm{B}_{n_2} \xrightarrow{k_{\mathrm{t}}(8)} (\mathrm{A}_{n_1}\mathrm{B}_{n_2})^{*}+q\,\mathrm{A}_{p_1}\mathrm{B}_{p_2+1}\ .
\end{array}\right\} \qquad (\mathrm{III})$$

Here q^{*} is the active polymerisation centre, the nature of which will henceforth be of little interest to us, i.e. it can be an anion, a cation, a radical, a biradical, etc. and L(3) and L(4), L(5), and L(6) are inactive molecules, the reactions with the rate constants $k_{\mathrm{t}}(3)$, $k_{\mathrm{t}}(4)$, $k_{\mathrm{t}}(5)$, and $k_{\mathrm{t}}(6)$ occurring in systems where copolymerisation proceeds via a radical mechanism; λ is the kinetic chain "terminating agent". The remaining symbols are self-evident and do not require additional explanation. In describing the termination of kinetic chains with the rate constant $k_{\mathrm{t}}(3)$, $k_{\mathrm{t}}(4)$, $k_{\mathrm{t}}(5)$, and $k_{\mathrm{t}}(6)$, we deliberately did not specify in a concrete form the corresponding reactions (recombination or disproportionation) in order to maintain a unique treatment, because this is unimportant for the subsequent description of the data.

This formulation of the copolymerisation mechanism (I)–(II)–(III) takes into account, in principle, the following factors: (1) the occurrence of reversible processes[17]; (2) the influence of the nature of the preterminal units on the propagation rate constants[18] (the mechanism can be extended without much difficulty by taking into account the influence of the nature of four- and five-unit sequences of monomeric fragments on the kinetic constants[19,20]); (3) the chain transfer reactions with the rate constants $k_{\mathrm{t}}(7)$ and $k_{\mathrm{t}}(8)$; nor does one exclude the possible influence of the degree of polymerisation and composition of macroradicals (or macroions) on the rate constants for the individual reactions in stage (II). Naturally, the characteristics of the synthesis via mechanism (I)–(II)–(III) depend significantly on a number of other factors, such as the active parameters of the reaction medium R_{i}, the temperature of the synthesis T, and a whole series of other parameters (they will be designated by P_{r}). It is already seen from mechanism (I)–(II)–(III) that in the synthesis of an *ensemble* of copolymer macromolecules the following parameters vary in the general case: the composition of the macromolecules α_{A}; the configuration of the macromolecules characterised by the composition parameter γ_{AB}; the average degree of polymerisation. It is noteworthy that the molecular weight and the nature of the molecular weight distribution[21,22] are not specific criterial parameters of binary statistic copolymerisation (naturally the choice of parameters is based on emphasising the differences between copolymerisation and homopolymerisation) and for this reason we shall henceforth use these parameters only when necessary.

Thus the fundamental (criterial) parameters of statistical polymerisation are assumed to be the "instantaneous" values of α_A and γ_{AB}, the distribution curves with respect to composition (w_{α_A}) and structure (configuration) ($w_{\gamma_{AB}}$) for the *ensemble* of the copolymer macromolecules with finite values of ψ. Naturally α_A, γ_{AB}, w_{α_A}, and $w_{\gamma_{AB}}$ are statistical characteristics and depend on many "instantaneous" parameters of the system. In particular, for copolymerisation processes which obey the (I)–(II)–(III) mechanism, we have

$$\begin{gathered}\alpha_A = F_1(\beta_A^0, R_i, P_r, T, k_{1AA}, k'_{1AA}, k_{1AB}, k'_{1AB}, k_{1BA}, k'_{1BA}, k_{1BB}, k'_{1BB} \,..\\ \ldots\, k_{nAAA}, k'_{nAAA}, k_{nBAA}, k'_{nBAA}, k_{nAAB}, k'_{nAAB}, k_{nBAB}, k'_{nBAB}, k_{nBBA},\\ k'_{nBBA}, k_{nABA}, k'_{nABA}, k_{nBBB}, k'_{nBBB}, k_{nABB}, k'_{nABB}\ ,\end{gathered} \tag{1}$$

where β_A^0 is the content of component A by weight in the initial monomer mixture and, when the expression in round brackets is denoted by $M_{B,i,m}$, we have

$$\gamma_{AB} = F_2(M_{P,i,m}), \tag{2}$$

$$w_{\alpha_A} = F_3\{M_{P,i,m}, \psi, k_t(7), \ k_t(8)\ \}, \tag{3}$$

$$w_{\gamma_{AB}} \doteq F_4\{M_{P,i,m}, \psi, k_t(7),. \ k_t(8)\ \}, \tag{4}$$

$$w_{\alpha_A, \gamma_{AB}} = F_5\{M_{P,i,m}, \psi, k_t(7), \ k_t(8)\ \}. \tag{5}$$

Eqns. (3)–(5) have been formulated for systems where interchain exchange reactions[22] or reactions involving kinetic chain transfer to macromolecules, particularly with rupture of the latter[23], take place. One should note that the functions F_3, F_4, and particularly F_5 contain incomparable more information about the copolymerisation process than the functions F_1 and F_2, because F_3, F_4, and F_5 take into account the influence of the polymer formed during the reaction (this is formally taken into account by introducing Ψ). The determination of the functions F_1 and F_2 and even more so F_3, F_4, and F_5 in an explicit form makes it necessary to overcome major technical difficulties even for the simplest copolymerisation models and, when the process becomes more complex, the difficulty of determining functional relations of type (1)–(5) increases significantly. There is no doubt that the determination of F_1, F_2, F_3, F_4, and F_5 in an analytical form is by no means possible, in principle, for all copolymerisation models.

Another method of analysing the copolymerisation process (which does not involve the determination of F_1, F_2, F_3, F_4, and F_5 in an explicit form), where a comparative analysis of experimental relations of the type $\alpha_A = f(\beta_A^0)$ and $\gamma_{AB} = f_1(\beta_A^0)$ is carried out in conformity with the characteristics of the "blank" (classical) system, is therefore more promising[4]. Naturally analysis of copolymerisation at the level of distribution curves with respect to composition for different β_A^0 and ψ is laborious and complex, but the reliability of such analysis is incomparable greater than that of the analysis of composition diagrams of the chemical structure of macromolecules for $\psi \to 0$,[4,24-26] which makes up for all the difficulties in the corresponding experiments. At any rate (both in the interpretation of data for distribution with respect to composition and in the analysis of the average compositions for different polymerisation increments[22]) the necessity for comparing the experimental results with data for the "blank" (classical) system immediately gives rise to a self-evident requirements—an integral part of the analysis must be a comprehensive study of various characteristics of the copolymerisation of classical systems.

III. TOPOLOGICAL SCHEMES FOR BINARY STATISTICAL COPOLYMERISATION

In analysing experimental data for copolymerisation, it is useful to distinguish four types of systems[4,8]: classical systems; classical systems subject to definite boundary conditions; "unusual" systems of the first and second kind.

1. Classical Systems

Assuming that the quasi-steady-state condition holds, Mayo and Lewis[27] and somewhat later Wall[28] derived a relation between the composition of the initial monomer mixture and the composition of the macromolecules formed in terms of two copolymerisation constants:

$$r_A = k_{AA}/k_{AB} \text{ and } r_B = k_{BB}/k_{BA}:$$

$$\frac{M_A}{M_B} = \frac{m_A}{m_B} \cdot \frac{r_A m_A + m_B}{r_B m_B + m_A}, \tag{6}$$

where M_A, M_B, m_A and m_B are the molar concentrations of monomers A and B in the copolymer macromolecules and in the initial mixture respectively. We may recall that Mayo and Lewis quite correctly referred to r_A and r_B as activity ratios and the name copolymerisation "constants" was given to them later. However, this seemingly purely terminological nicety later led to serious confusion in both the kinetic and statistical copolymerisation theories let alone applications such as the synthesis of copolymers "with specified properties". In 1944 Eqn. (6) was obtained by Goldfinger and Kone[29] without postulating the quasi-steady-state condition. On conversion to weight concentrations, the Mayo–Lewis equation [Eqn.(6)] becomes

$$\frac{g\alpha_A\,(1-\beta_A^2)}{(1-\alpha_A)\,\beta_A^2}\,r_B - r_A = \frac{1-\beta_A}{\beta_A}\left(g - \frac{\alpha_A}{1-\alpha_A}\right), \tag{7}$$

where $\alpha_A = 1 - \alpha_B$, $\beta_A = 1 - \beta_B$, and g is the ratio of the molecular weights of components A and B. In the first place, one should note that Eqns. (6) and (7) are by no means valid for all copolymerisation models[4,8] and, when the process takes place within the framework of classical relations (r_A = const. and r_B = const.), it is necessary that many special conditions should be fulfilled. We shall formulate them here, because they are important:

(1) the chain propagation reactions must be fully irreversible, i.e.

$$\begin{gathered}k'_{AA} = k'_{AB} = k'_{BB} = k'_{BA} \ \ldots\ = k'_{nAAA} = k'_{nBAA} =\\ = k'_{nAAB} = k'_{nBAB} = k'_{nABA} = k'_{nBBB} = k'_{nABB} = 0;\end{gathered}$$

(2) the monomers A and B must be capable of polymerising via only one mechanism, i.e. a one-centre copolymerisation process must take place:

(3) the propagation rate constants must be independent of the composition of the initial monomer mixture, i.e.

$$\begin{gathered}k_{nAA} \neq \mathrm{f}(\beta_A^0),\ k_{nBB} \neq \mathrm{f}(\beta_A^0);\ \ k_{nAB} \neq \mathrm{f}(\beta_A^0);\\ k_{nBA} \neq \mathrm{f}(\beta_A^0);\end{gathered}$$

(4) the copolymerisation process must be homophase with respect to all β_A^0 and ψ;

(5) the propagation rate constant must be independent of the degree of polymerisation, i.e.

$$k_{1AA} = k_{2AA} = \ldots k_{nAA};\; k_{1BB} = k_{2BB} = \ldots k_{nBB};$$
$$k_{1AB} = k_{2AB} = \ldots k_{nAB};\; k_{1BA} = k_{2BA} = \ldots k_{nBA};$$

(6) the propagation rate constants must be independent of the composition of the macroradical (macroion), in particular the propagation rate constants must be independent of the nature of the preterminal, pre-preterminal and more remote units, i.e.

$$k_{nBAA} = k_{nAAA};\; k_{nBAB} = k_{nAAB};$$
$$n_{nABB} = k_{nBBB};\; k_{nBBA} = k_{nABA};$$

(7) the polymer formed must not influence the parameter of the interactions of macroradicals (macroions) with the monomers A and B, i.e.

$$k_{nAA} \neq f(\psi);\; k_{nAB} \neq f(\psi);\; k_{nBA} \neq f(\psi);\; k_{nBB} \neq f(\psi);$$

(8) the reactions involving the transfer of the kinetic chain to the macromolecules, i.e.

$$k_t(7) = k_t(8) = 0;$$

must not occur during the synthesis;

(9) the lifetimes of the individual macroradicals must be much shorter than the times of formation of the polymerisation increment[20], i.e. there should be no long-lived active centres in the system and hence bimolecular termination reactions with the constants $k_t(3)$, $k_t(4)$, $k_t(5)$, and $k_t(6)$ [see the mechanism (I)–(II)–(III)] must be ruled out in the case where $p_1/p_2 \neq m_1/m_2$;

(10) the system must be free from active ingredients (in the simplest case complex-forming additives) which bind part of the monomer A or B; this condition can be represented schematically as follows:

$$aA + Q \not\rightarrow a'\overset{+}{A} + (a - a')A,$$
$$bB + Q \not\rightarrow b'\overset{+}{B} + (b - b')B,$$
$$aA + bB \not\rightarrow a'(AB)^+ + (a - a')B + (b - a')B;$$

It is postulated that the relative activities of A and B, on the one hand, and A^+, B^+, and $(AB)^+$, on the other, in copolymerisation reactions differ significantly from one another;

(11) it is assumed that the copolymerisation process should involve the formation of products with fairly high molecular weights; at any rate the degree of copolymerisation is such that the influence of the terminal units may be neglected;

(12) a microsubstrate with the composition β'_A, different from that of the macroscopic composition β_A, must not be formed around the macroradicals (or macroions); in other words, in the system there must be no selective macroradical–monomer A (or B) interactions responsible for the appearance of microheterophase properties[30-33].

When all twelve necessary conditions are fulfilled, the copolymerisation process is greatly simplified, but the main bulk of the information about the system may be obtained using only two parameters, namely r_A = const. and r_B = const. In conformity with the aim of the present review, it is appropriate to list at this point the decisive features of classical polymerisation which make it possible to distinguish a classical process from an unusual process.

1. In order to obtain relations (1)–(5) in an explicit form, it is in principle sufficient to operate with two process parameters, namely r_A = const. and r_B = const.

2. There is an unambiguous relation between α_A and β_A for any β^0_A and ψ. In an analytical form the relation $\alpha_A = f(\beta^0_A)$ is determined by the Mayo–Lewis equation (6) or (7). Fig. 1 illustrates schematically the relation between α_A and β_A for systems with and without an azeotropic point. For classical systems, a single rigorously defined value of α_A corresponds to each β_A, i.e. we have $\beta'_A \longleftrightarrow \alpha'_A(1)$, $\beta''_A \longleftrightarrow \alpha''_A(1)$, and $\beta'''_A \longleftrightarrow \alpha'''_A(1)$ for curve *1*, $\beta'_A \longleftrightarrow \alpha'_A(2)$, $\beta''_A \longleftrightarrow \alpha''_A(2)$, and $\beta'''_A \longleftrightarrow \alpha'''_A(2)$ for curve *2*, and $\beta'_A \longleftrightarrow \alpha'_A(3)$, $\beta''_A \longleftrightarrow \alpha''_A(3)$, and $\beta'''_A \longleftrightarrow \alpha'''_A(3)$ for curve *3*.

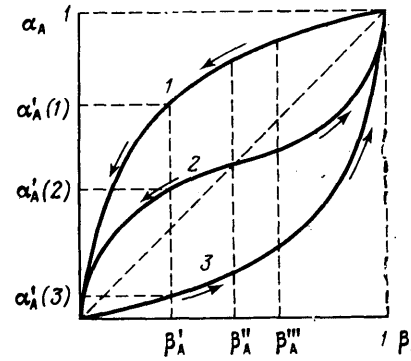

Figure 1. Schematic composition diagrams for systems with (curve *2*) and without (curves *1* and *3*) azeotropic points: 1) $r_A(1) > 1$, $r_B(1) < 1$; 2) $r_A(2) < 1$, $r_B(2) < 1$ or a less probable version of the synthesis with $r_A(2) > 1$, $r_B(2) > 1$; 3) $r_A(3) < 1$, $r_B(3) > 1$.

3. For each point on the composition diagram, it is possible to predict the direction of the development of the process, i.e. the increase or decrease of α_A when ψ increases. Thus, for the process described by curve *1* in Fig. 1, α_A diminishes, while that for the process described by curve *3* increases with increase of ψ. The above relations are valid for any fixed β^0_A = const. As regards systems with an azeotropic point (curve *2*), it is necessary to distinguish three regions: the first region, involving a decrease of α_A for $\beta_A < \beta''_A$, the second, involving an increase of α_A when $\beta_A > \beta''_A$, and the third, where $\alpha_A = \alpha''_A(2) \neq f(\psi)$ for $\beta_A = \beta''_A$; in all cases the analysis is carried out on the assumption of a continuous increase of ψ. To make the analysis complete, we may also note the special case where $r_A = r_B = 0$.[12,34] Naturally, in such systems the compositions of the macromolecules formed are the same for all β^0_A and ψ and for this reason no particular direction of process development can be specified and we are dealing in essence with a homopolymer $(AB)_n$ for any β^0_A and ψ.

4. It can be shown (this is done most simply using a model composition diagram) that for classical systems any interpretation of data in terms of the $\alpha_A = f(\beta_A)$ relation leads to the same values of r_A and r_B.[35,36]

5. The relative errors in the determination of r_A and r_B (i.e. $\Delta r_A/r_A$ and $\Delta r_B/r_B$) are objective characteristics of the copolymerisation process and depend mainly on the

experimental technique; the method of determination itself and the absolute values of r_A and r_B have less effect[10,26].

6. Using two copolymerisation constants (r_A and r_B), it is possible to plot theoretical integral distribution curves with respect to composition (IDCC) for classical systems whatever the values of β_A^0 and ψ, both by the Skeist method[37] and, with the aid of analytical expressions for $1-\psi$, by the Meyer and Lurry method[38] (for molar IDCC) or its analogue for the derivation of weight distribution functions with respect to composition[39]. As an illustration, Fig. 2 presents calculated and experimental IDCC for one of the systems[40]. One should note a characteristic property of classical IDCC—for each individual point corresponding to fixed α_A^0, it is possible to determine β_A^0 and ψ^0, provided that the overall ψ is known for the IDCC.

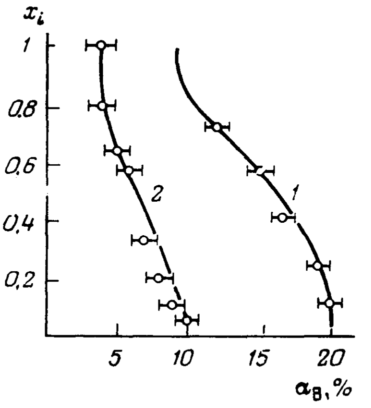

Figure 2. Theoretical and experimental IDCC for the vinyl acetate (A)–vinylcaprolactam (B) system; the theoretical IDCC are indicated by continuous lines[40]: 1) $\beta_A^0 = 0.16$; 2) $\beta_B^0 = 0.05$; x_i is the integral proportion by weight of the ith fraction.

7. For classical systems, operation (6) is reversible, i.e. using IDCC it is possible to determine r_A and r_B by an appropriate treatment of data (for example, in terms of the variables[41]

$$\frac{\beta_A}{1-\beta_A}\left(g-\frac{1-\alpha_A}{\alpha_A}\right)-\frac{\beta_A^2(1-\alpha_A)}{\alpha_A(1-\beta_A)^2},$$

where g is the ratio of the molecular weights of component A and B). It is of interest that, in order to derive r_A and r_B from IDCC, only one distribution curve with respect to composition is in principle sufficient. Fig. 3 presents an example of the determination of r_A and r_B from IDCC for the acrylamide–sodium fumarate system with added NaCl; according to the data in Fig. 3, $r_A = 10$ and $r_B = 0$.

8. There is an unambiguous relation between all the distribution curves with respect to composition within the given "family"[43] (i.e. for the set of IDCC, where r_A = const. and r_B = const.), which makes it possible to apply the principle of extrapolation and superposition in analysing the set of IDCC for different β_A^0 and ψ.

We shall consider this in greater detail, since the extrapolation and superposition principles mentioned above are common to classical systems and their breakdown can serve as direct evidence for the appearance of "unusual" relations in the system. We shall assume a system without an azeotropic point (Fig. 4, curve *2*); in this case the content of the second component decreases with increase of ψ. Accordingly, the copolymerisation process may be characterised statistically by a family of monotonically varying distribution functions with respect to composition. The principle of the interrelation of the distribution curves with respect to composition was first clearly formulated by Markert[44,45], who illustrated such an interrelation by analysing the differential distribution curves with respect to composition (DDCC). However, in the comparative analysis of distribution curves with respect to composition it is much more convenient to employ IDCC rather than DDCC and to carry out the corresponding analysis using weight distribution functions with respect to composition. Evidently in the case of IDCC there is an unambiguous relation between the individual curves of a single "family". The fundamental condition for the existence of such a relation is that fractions having the same composition may be obtained for different compositions of the initial monomer mixture at different copolymerisation stages.

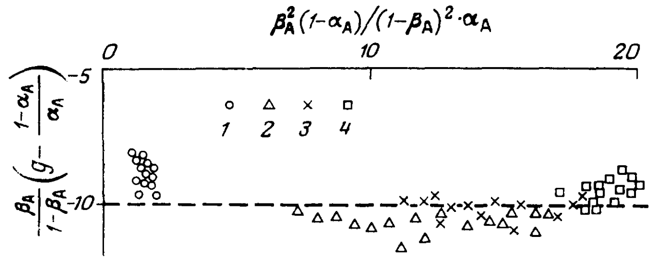

Figure 3. Dependence of $[\beta_A(1-\beta_A)][g-(1-\alpha_A)/\alpha_A]$ on $\beta_A^2(1-\alpha_A)/\alpha_A(1-\beta_A)^2$ for the acrylamide–sodium fumarate system with added 10% NaCl;[42] β_B^0: 1) 0.1; 2) 0.4; 3) 0.5; 4) 0.67.

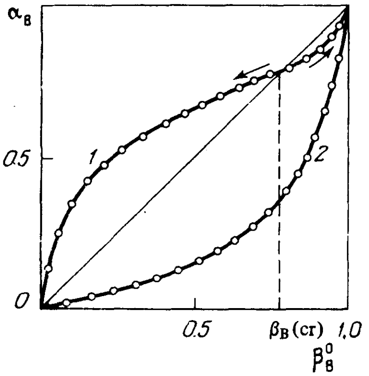

Figure 4. Composition diagrams for copolymerisation models: 1) $r_A = 0.1$, $r_B = 0.7$, $g = 0.8$; 2) $r_A = 7.0$, $r_B = 0.09$, $g = 1.63$.[43]

The interrelation between the individual IDCC of a single "family" can be most simply illustrated using as an example the dependence of $1 - \psi$ on β_A. Analytical weight functions relating $1 - \psi$ to r_A, r_B, g and β_A have been obtained[39]. Fig. 5 presents the calculated relations[43] between $1 - \psi$ and β_A for two copolymerisation models, whose composition diagrams are illustrated in Fig. 4. Simple comparison of the curves in Fig. 5 already shows that there is a simple relation between individual curves. It is easy to establish in an explicit form also the nature of the relations between the individual curves in Figs. 5*a* and 5*b*.[43]. Thus curves *2–6* in Fig. 5*b* as it were describe the part of the copolymerisation process illustrated by curve *1*; similarly curves *3–6* constitute, as it were, part of curve *2*, etc. Curve *2*, for example, describes the same process as curve *1* after the attainment of a definite degree of conversion $\psi_a = 0.27$; similarly curves *3–6* are part of curve *1* after the attainment of values of ψ_a of 0.44, 0.58, 0.73, and 0.76 respectively. Thus, after the attainment of ψ_a, the curves of one "family" differ only by a scale factor, which in the given instance is ψ. The validity of such comparison of the IDCC of a single family is confirmed by the satisfactory correspondence between the individual calculated points and curves evaluated directly from an analytical expression for $1 - \psi$.[39]

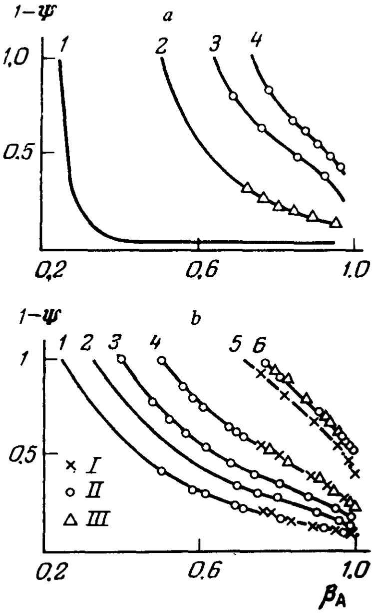

Figure 5. Dependence of $1 - \psi$ on β_A for blank systems[43]: *a*) $r_A = 0.1$, $r_B = 0.7$, and $g = 0.8$ (Lewis and Young[46]) for $\beta_A^0 = 0.25$ (curve *1*), 0.5 (curve *2*), 0.65 (curve *3*), and 0.75 (curve *4*); *b*) $r_A = 7.0$, $r_B = 0.09$, and $g = 1.63$ for $\beta_A^0 = 0.75$ (curve *1*), 0.68 (curve *2*), 0.6 (curve *3*), 0.5 (curve *4*), 0.27 (curve *5*), and 0.25 (curve *6*). Points I, II, and III were obtained using different computational formulae.

Clearly the correlation between the individual curves for the dependence of $1 - \psi$ on β_A inevitably implies the existence of an unambiguous relation also between the IDCC. This may be illustrated by Fig. 6. The individual points in the figure were obtained using the extrapolation and superposition principles for the comparison of the IDCC.[43] Evidently the correspondence of the IDCC obtained by the Skeist method and by the application of the extrapolation and superposition relations[43] is entirely satisfactory. This factor, demonstrating the particular advantage of the application of the superposition principle, may be employed for the rapid construction of IDCC for classical systems. The principles described are extremely important also in the comparative analysis of the set of experimental IDCC for which there can be no simple correlation between the individual curves, which may be an indication of the "unusual" nature of the process.

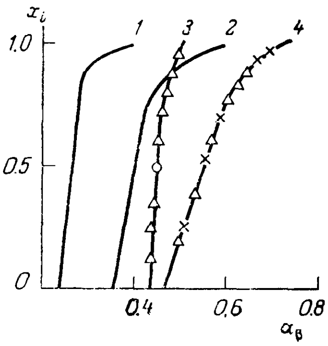

Figure 6. The IDCC for the system with $r_A = 0.1$, $r_B = 0.7$, and $g = 0.8$ (Myagchenkov and Frenkel'[41]); β_A^0: 1) 0.25; 2) 0.5; 3) 0.67; 4) 0.75. The continuous curves were obtained by the Skeist method and the individual points were obtained using the extrapolation and superposition relations between the IDCC.[42]

9. For classical systems, the chemical structure of macromolecules (it can be regarded as known, provided that the probabilities of the occurrence of various sequences of the monomeric fragments A and B are known[47–49]) is determined unambiguously by the values of r_A and r_B.

10. Knowing the chemical structures for different β_A^0, it is possible to calculate r_A and r_B for classical systems.

11. There is no doubt about the existence of an unambiguous relation between IDCC and the stereochemical configuration of the copolymer macromolecules.

12. For classical systems, there is an unambiguous relation between the IDCC, the chemical structure of the *ensemble* of macromolecules, and the quantitative parameters of the inhomogeneity with respect to composition[50].

13. For classical systems, the specimen should be monodisperse with respect to composition at the azeotropic point $\beta_A^0 = \beta_A(\text{az.})$, i.e. $\alpha_A = \beta_A(\text{az.})$ in the region $0 \leq \psi \leq 1$.

Thus an unambiguous relation between β_A, α_A, the chemical structure (configuration) of the macromolecules, the IDCC, and the quantitative parameters of the inhomogeneity with respect to composition is characteristic of classical systems. The breakdown of the correspondences 1–13 already constitutes indirect evidence for the lack of validity of the description of the copolymerisation process with the aid of two copolymerisation constants r_A = const. and r_B = const.

2. Systems Which Reduce to Classical Systems when Definite Boundary Conditions are Fulfilled

In such systems none of the twelve conditions necessary for the classical process are fulfilled, but the nature of the process itself remains such that one may expect the fulfilment of all thirteen features of a classical process, enumerated above, for a definite range of β_A^0 and ψ values. We shall consider several systems of this kind.

1. All the conditions necessary for a classical process are fulfilled with the exception of the seventh condition and the influence of the polymer formed on the rate constants for the propagation of macromolecules may be traced only after the attainment of a certain value ψ_{cr}, which depends on β_A^0. Suppose that $\beta_A^0(1)$, $\beta_A^0(2)$, $\beta_A^0(3)$ ... $\beta_A^0(p)$ correspond to $\psi_{cr}(1)$, $\psi_{cr}(2)$, $\psi_{cr}(3)$, ..., $\psi_{cr}(p)$ and that $\psi_{cr}(1) < \psi_{cr}(2) < \psi_{cr}(3) < \ldots \psi_{cr}(p)$, while the values of $\beta_A^0(1) - \beta_A^0(p)$ cover virtually the entire range of β_A^0 from 0 to 1; in this case the system may be regarded as classical for the degrees of conversion $\psi < \psi_{cr}(1)$.

2. All the conditions necessary for a classical process hold with the exception of the tenth condition, but the concentration of active ingredients is such that the entire monomer A (or B) is converted into A^+ (or B^+), i.e. $mA + Q \rightarrow mA^+$ (or $mB + Q \rightarrow mB^+$). In this case the copolymerisation reaction takes place between B and A^+ (or A and B^+) and one may expect a change in the copolymerisation constants $r_A \rightarrow r_{A^+}$ or $r_B \rightarrow r_{B^+}$, but such changes do not entail the failure of even one of the thirteen features of a classical process.

3. The separation of the system into separate phases occurs only for certain values of $\beta_A \geq \beta_A(\text{cr.})$. Complications of this kind in the copolymerisation process can be readily traced in the copolymerisation of acrylamide with hydrophilic non-ionogenic monomers (solvent—water)[50-54].

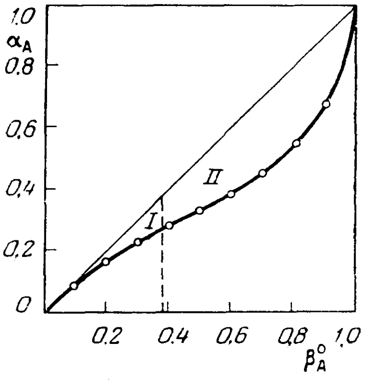

Figure 7. Composition diagram for statistical acrylonitrile–hydroxymethylmethacrylamide copolymers[54].

Fig. 7 presents a typical composition diagram for the acrylonitrile (A)–hydroxymethylmethacrylamide (B) system[54]. There are two characteristic regions in the diagram: region I where the copolymerisation process takes place in a single phase and region II where the copolymerisation takes place in a two-phase system. Clearly in region I (i.e. for $\beta_A \leq 0.39$) the system can manifest all the features characteristic of a classical process and in the region $0 \leq \beta_A \leq 0.39$ it is possible to calculate r_A and r_B. On the other hand, in region II the system is known to be non-classical and it is therefore erroneous to operate with the values of r_A and r_B found for region I; in general for region II one can speak in this instance only of apparent copolymerisation "constants" r_A^* and r_B^* [8,55]. One must bear in mind that systems where the copolymerisation process takes place in a single phase only within a certain region of β_A values are encountered fairly frequently in practice[1].

4. An analogous limitation may be observed also when reactions involving chain transfer to macromolecules occur in the system. If ψ_{cr} is a minimum value of ψ (for different compositions of the initial polymer mixture) after the attainment of which reactions involving the transfer of kinetic chains to macromolecules are observed, then the system may be regarded as classical in the region $0 \leq \psi \leq \psi_{cr}$. However, the extension of the observed relations (for example, the use of values of r_A and r_B found for the region $0 \leq \psi < \psi_{cr}$) to the region $\psi_{cr} \leq \psi \leq 1$ is known to be illegitimate and may lead to serious errors in the estimates of the characteristics of the statistical copolymerisation process.

3. Unusual Systems of the First Kind

One or several of the necessary conditions for a classical process do not hold for such systems, but there is an unambiguous relation between β_A and α_A for all the β_A^0 and ψ. The nature of the $\alpha_A = f(\beta_A)$ relation is more complex than the Mayo–Lewis equation; at any rate, this relation cannot be described in terms of only two copolymerisation constants. In the majority of cases it is possible to plot calculated distribution curves with respect to composition for unusual systems of the first kind (and hence it is possible to evaluate the quantitative parameters of the inhomogeneity with respect to composition) and to find analytical expressions for the functions characterising the structure of the macromolecules, but these relations are much much complex than the corresponding relations for classical systems. Naturally, not all of the thirteen enumerated features of classical polymerisation hold for unusual systems of the first kind. There is no doubt that the study of the relations $\alpha_A = f(\beta_A)$ can serve only as a first approximation in the analysis of the process characteristics for unusual systems of the first kind; for a more accurate assessment of the process, it is necessary to compare theoretical and experimental IDCC and to analyse the chemical structure of the copolymer macromolecules.

(1) The fulfilment of all the necessary conditions for classical copolymerisation with the exception of the sixth condition, i.e. that the reactivity of the macroradical depends on the nature of the free terminal and more remote units, is characteristic of the system[1,18-20,56,57]. A number of workers[1,18-20,56,57] explained the deviation of the $\alpha_A = f(\beta_A^0)$ relations from the classical relations (6) and (7) by the fact that r_A and r_B do not reflect fully the specific features of the interaction in the macroradical (macroion)–monomer system. When account is taken of the influence of the pre-terminal units, the following relation must be formulated instead of the Mayo–Lewis equation:

$$\frac{M_A}{M_B} = \frac{1 + (r'_A m_A/m_B)(r_A m_B/m_A + 1)/(r'_A m_A/m_B + 1)}{1 + (r'_B m_B/m_A)[(r_B + m_A/m_B)/(r'_B + m_A/m_B)]}, \qquad (8)$$

where

$$r_A = k_{AAA}/k_{AAB};\quad r'_A = k_{BAA}/k_{BAB};$$
$$r_B = k_{BBB}/k_{BBB};\ r'_B = k_{ABB}/k_{ABA}.$$

For the pre-terminal model, Eqn.(8) becomes even more complex and the relation between α_A and β^0_A is expressed in terms of eight copolymerisation constants:

$$r_A = k_{AAAA}/k_{AAAB};\quad r_B = k_{BBBB}/k_{BBBA};$$
$$r'_A = k_{BAAA}/k_{BAAB};\quad r'_B = k_{ABBB}/k_{ABBA};$$
$$r''_A = k_{ABAA}/k_{ABAB};\quad r''_B = k_{BABB}/k_{BABA};$$
$$r'''_A = k_{BBAA}/k_{BBAB};\quad r'''_B = k_{AABB}/k_{AABA}.$$

Analytical expressions have been obtained[20] for the relation $\alpha_A = f(\beta^0_A)$ taking into account also more remote interactions (via four- and five-unit sequences of monomer fragments). Thus, according to Barb[58], $r_A = 0.0084$, $r'_A = 0.01$, $r''_A = 0.0275$, and $r'''_A = 0.063$ for the styrene–maleic anhydride system; this set of constants describes satisfactorily the experimental relation $\alpha_A = f(\beta^0_A)$. We may note that a set of constants of the type r_A, r'_A, r''_A, r'''_A, r_B, r'_B, r''_B, r'''_B may be regarded as resembling variational parameters which establish the correspondence between the experimental points on the composition diagram. It is appropriate to note here that the use of a large set of such constants makes it possible, in principle, to describe satisfactorily very complex relations $\alpha_A = f(\beta^0_A)$, but the lack of reasonable correlations between r_A, r'_A, r''_A, r'''_A, on the one hand, and r_B, r'_B, r''_B, r'''_B, on the other, is an indication of the inaccuracy and arbitrary nature of such an approach. We believe that the region of the applicability of the pre-terminal model must be clearly defined—this model must not be misused when difficulties arise in finding an explanation for the sharp differences between the values of r_A and r'_A, on the other hand, and r_B and r'_B, on the other.

It is necessary to consider yet another question. It has been shown[59] that analysis of IDCC and of the variance of the distribution with respect to composition in relation to analysis of the function $\alpha_A = f(\beta^0_A)$ makes it possible to infer with much greater certainty which model (classical or pre-terminal) is valid in each specific case of copolymerisation.

(2) Systems where all the necessary conditions for classical copolymerisation hold with the exception of the tenth condition, but the reactivities of the activated [A^+ (or B^+)] and non-activated specimens [A (or B)] monomers do not differ sufficiently to entail the appearance of an ambiguity in the relation $\alpha_A = f(\beta^0_A)$. Without infringing the generality of the description, we shall assume that the activated monomer (in the simplest case a monomer bound in a complex) is monomer A. In such a system the copolymerisation process may be described by the Alfrey–Goldfinger scheme[60] for a three-component mixture of monomers:

$$\begin{aligned}
&A_{n-q-1}B_qA^\bullet + A \xrightarrow{k_{AA}} A_{n-q}B_qA^\bullet;\\
&A_{n-q-1}B_qA^\bullet + A^+ \xrightarrow{k_{AA+}} A_{n-q}B_q(A^+)^\bullet,\\
&A_{n-q-1}B_qA^\bullet + B \xrightarrow{k_{AB}} A_{n-q}B_qB^\bullet,\\
&A_{n-q-1}B_q(A^+)^\bullet + A \xrightarrow{k_{A+A}} A_{n-q-1}B_qA^+A^\bullet,\\
&A_{n-q-1}B_q(A^+)^\bullet + A^+ \xrightarrow{k_{A+A+}} A_{n-q-1}B_qA^+(A^+)^\bullet,\\
&A_{n-q-1}B_q(A^+)^\bullet + B \xrightarrow{k_{A+B}} A_{n-q-1}B_qA^+B^\bullet,\\
&A_{n-q-1}B_qB^\bullet + A \xrightarrow{k_{BA}} A_{n-q-1}B_{q+1}A^\bullet,\\
&A_{n-q-1}B_qB^+ + A^+ \xrightarrow{k_{BA+}} A_{n-q-1}B_{q+1}(A^+)^\bullet,\\
&A_{n-q-1}B_qB^\bullet + B \xrightarrow{k_{BB}} A_{n-q-1}B_{q+1}B^\bullet.
\end{aligned}\qquad (9)$$

The composition equation becomes

$$\begin{aligned}
\mathrm{d}M_A : \mathrm{d}M_B : \mathrm{d}M_{A^+} = M'_A\left[\frac{M'_A}{r_{A^+A}r_{BA}} + \frac{M_B}{r_{BA}r_{A^+B}} + \frac{M_A - M'_A}{r_{A^+A}r_{A^+B}}\right]\times\\
\times\left[M'_A + \frac{M_B}{r_{AB}} + \frac{M_A - M'_A}{r_{AA^+}}\right] : M_B\left[\frac{M_A}{r_{AB}r_{A^+A}} + \frac{M_B}{r_{AB}r_{BA^+}} + \right.\\
\left. + \frac{M_A - M'_A}{r_{A^+B}r_{AA^+}}\right]\left[M_B + \frac{M'_A}{r_{BA}} + \frac{M_A + M'_A}{r_{BA^+}}\right] : (M_A - M'_A)\times\\
\times\left[\frac{M'_A}{r_{AA^+}r_{BA}} + \frac{M_B}{r_{BA^+}r_{AB}} + \frac{M_A - M'_A}{r_{AA^+}r_{BA^+}}\right]\times\\
\times\left[(M_A - M'_A) + \frac{M'_A}{r_{A^+A}} + \frac{M_B}{r_{A^+B}}\right],
\end{aligned}$$

where M'_A and M_A are respectively the molar concentration of the monomer A not bound in the complex and the overall concentration of the same monomer A in the system (it is implied that M_A and M'_A are known) and $\mathrm{d}M_A$, $\mathrm{d}M_B$, and $\mathrm{d}M_{A^+}$ are the numbers of molecules of A, B, and A^+ in the copolymer macromolecule:

$$r_{AB} = \frac{k_{AA}}{k_{AB}};\quad r_{AA^+} = \frac{k_{AA}}{k_{AA^+}};\quad r_{BA} = \frac{k_{BB}}{k_{BA}};$$
$$r_{BA^+} = \frac{k_{BB}}{k_{BA^+}};\quad r_{A^+A} = \frac{k_{A^+A^+}}{k_{A^+A}};\quad r_{A^+B} = \frac{k_{A^+A^+}}{k_{A^+B}}.$$

Naturally Eqn.(10) is applicable to the analysis of copolymerisation under the conditions of complex formation in the system only when there are definite relations between M_{A^+} and M'_A (in particular, when the concentration of A^+ is limited by the concentration of the complex-forming agent in the system). In order to determine r_{AB}, r_{AA^+}, r_{BA}, r_{BA^+}, r_{A^+B}, and r_{A^+A}, it is necessary to analyse the composition diagrams for the binary systems (AA^+, AB, BA^+). It is fairly difficult to carry out such analysis for the AA^+ system, but even in its absence it is clear that the copolymerisation process in a system with the monomer partly bound in a complex cannot be described by the classical Mayo–Lewis equation. For this reason, the values of r_A and r_B obtained by the usual treatment of the data (without taking into account the complex-formation steps) are apparent process characteristics, which has been shown[61] in relation to the copolymerisation of acrylic and methacrylic acids with vinylpyrrolidinone. In the same report it is correctly noted that calculation of the parameters Q and e in the Alfrey–Price equation for the above systems lacks significance. In principle, any instance of polymerisation where the monomers A and B form a complex (AB) which behaves in the copolymerisation reaction as an "individual monomer" can be reduced to a relation of type (10).

(3) Systems with weak depolymerisation reactions, i.e. those where there is a specific breakdown of the necessary first condition. In this case the relation $\alpha_A = f(\beta_A)$ cannot be described in terms of two copolymerisation constants r_A = const. and r_B = const. It is implied that depolymerisation is not sufficiently intense to cause the breakdown of the unambiguous nature of the relation $\alpha_A = f(\beta_A)$.

(4) Systems where all the necessary conditions for classical copolymerisation are fulfilled with the exception of the eleventh condition, i.e. in such systems the synthesis results in the formation of copolymer macromolecules with an average degree of polymerisation < 100. Such systems may be regarded as "defective" classical systems or, more precisely, as systems obtained by random degradation from quasi-infinite copolymer macromolecules for the same values of r_A, r_B, β^0_A, and ψ.[12] The breakdown of the classical relations between IDCC and the

chemical structure of the macromolecules is due to two causes: the statistical nature of the reactions involving the rupture of macromolecules and the necessity for the introduction of revised values of α_A and α_B taking into account the influence of terminal groups on these parameters. Naturally the distribution functions with respect to composition depend on n. There have been obtained in an analytical form [62,63] and the following most general formulation is possible:

$$w_{n,M_A} = A(1 - f + nf/B)\,n^{3/2}e^{-n/B}\exp[-n(M_A - \overline{M}_A)^2/D], \qquad (11)$$

where w_{n,M_A} is the weight fraction of macromolecules with the degree of polymerisation n and the composition, M_A, $\overline{M}_A = \sum_{i=1}^{k} N_i M_{Ai} / \sum_{i=1}^{k} N_i$ is the arithmetical mean composition of the statistical *ensemble* of k fractions of macromolecules, B the arithmetical mean degree of polymerisation, A and D are constants which depend on r_A and r_B, and f is the probability of recombination steps in the termination of kinetic chains ($f = 1 - f_1$, where f_1 is the probability of the occurrence of disproportionation reactions in the termination of kinetic chains).

(5) Systems with a varying reactivity of the monomers A and B; here the relation $\alpha_A = f(\beta_A)$ remains unambiguous for all β_A^0. Many of such systems can be reduced to non-steady-state systems of the type

$$r_A = c_0 + R\beta_A, \qquad (12)$$

$$r_B = c_0' + R'\beta_A, \qquad (13)$$

where c_0, c_0', R, and R' are constants. It can be shown that, for systems of type (12) and (13), it is possible to calculate the IDCC,[64] the parameters of the quantitative estimate of the inhomogeneity with respect to composition, and the probabilities of various sequences of AB units in the macromolecules for different β_A^0, and ψ.

We shall consider further specific instances of copolymerisation in systems where the reactivity of the monomers is variable. Systems where one of the monomers contains ionogenic groups are of greatest interest in this respect; the reactivity of the medium is then such that the ionogenic groups exist in partly or fully ionised states [65-67]. The characteristics of the copolymerisation of ionogenic monomers must be considered in greater detail for three reasons: (1) the great practical importance of polyelectrolytes [9,68], (2) the fact that such systems are convenient models for the analysis of non-steady-state versions of copolymerisation, and (3) the fact that the characteristics of the copolymerisation of ionogenic monomers have so far been inadequately investigated [4,9,69].

In the first place we may note that many complications arise even in the homopolymerisation of ionogenic monomers, due to the presence of charged groups in the macroradical and in the monomer [69-72]. Thus in the homopolymerisation of ionogenic monomers in ionising media the overall rate of the process [73], the activation energy, the molecular weight [9,74,75], the degree and nature of stereoregularity [47,74], and the order of the reaction with respect to the monomer [76] depend on pH and the ionic strength of the solution. The order of the reaction with respect to the monomer varies in ionising media as the dielectric constant [77] and the ionic strength of the solution [78] are altered. Presumably, on passing from high to very low concentrations of the ionogenic monomer, the order of the reaction with respect to the monomer does not remain constant. In addition, one may expect also the variability of the individual elementary "constants" when the concentration of the monomer is varied within wide limits. Indeed $k_p/k_0^{1/2} = f(c_A) \neq$ const., where k_p and k_0 are propagation and termination rate constants, was obtained [79] for concentrations of the ionogenic monomer (2-sulphoethylmethacrylate) $c_A < 2\%$. This implies that k_p and k_0 are variable for $c_A < 2\%$ and depend on the internal ionic strength set up by the ionogenic monomer A. The results of the above study [79] are important for a correct assessment of the mechanism of the polymerisation of ionogenic monomers.

Naturally, in the copolymerisation of monomers with ionogenic groups the above polymerisation anomalies must be manifested to an even greater extent. There are in addition new anomalies associated directly with the greater complexity of the copolymerisation mechanism. Indeed, even when the specific features of the macroradical (the nature of the ionisation of the terminal, pre-terminal, and pre-pre-terminal units and the overall charge of the macroion) are disregarded, the copolymerisation mechanism becomes

$$\begin{aligned}
&A_nB_m\dot{A} + A \xrightarrow{k_{AA}} A_nB_mA\dot{A},\\
&A_nB_m\dot{A} + (A) \xrightarrow{k_{A(A)}} A_nB_mA(\dot{A}),\\
&A_nB_m\dot{A} + B \xrightarrow{k_{AB}} A_nB_mA\dot{B},\\
&A_nB_m\dot{A} + A \xrightarrow{k_{BA}} A_nB_mB\dot{A},\\
&A_nB_m\dot{A} + (A) \xrightarrow{k_{B(A)}} A_nB_mB\dot{A},\\
&A_nB_m\dot{B} + B \xrightarrow{k_{BB}} A_nB_mB\dot{B}.
\end{aligned} \qquad (14)$$

where A is the ionised unit A. Clearly mechanism (14) is not equivalent to the Mayo–Lewis mechanism in view of the differences between the values of $k_{A(A)}$ and k_{AA}, on the one hand, and between $k_{B(A)}$ and k_{BA}, on the other. Together with the usual property (i.e. the property of the monomer) of an unsaturated compound, the ionised monomer forms a cloud of counterions (the Debye–Hückel "ionic atmosphere" [80,81]) around the ionised macroradical and, as ψ increases, the monomer A passes from the ionic atmosphere to the chain of the copolymer macromolecule. It is then necessary to take into account the fact that γ_{ion}'—the effective degree of ionisation of the A monomer fragment within the macromolecule—is by no means identical with γ_{ion}—the effective degree of ionisation of the monomer A. This is because within the macromolecule the strong electrostatic field of the counterions (we may state that within the macromolecule their concentration is much higher than the average concentration of the counterions in the bulk of the solution) lowers the effective ionisation constant, so that $\gamma_{ion}' < \gamma_{ion}$. If (A) is a univalent ion and an electrolyte maintaining a constant ionic strength is absent from the copolymerising system, one can show [10] that the effective ionic strength I_{eff} for $\psi = \psi_1$ is

$$I_{eff}(\psi_1) = ac_A\{\gamma_{ion}(1 - \psi_1) + \gamma_{ion}'\psi_1\}. \qquad (15)$$

For $\psi = 0$, we have

$$I_{eff}^0 = a\gamma_{ion}c_A, \qquad (16)$$

where $a = 500/M_0$ and M_0 is the molecular weight of the monomer A. If

$$R \equiv I_{eff}(\psi_1)/I_{eff}^0 = [\gamma_{ion}(1 - \psi_1) + \gamma_{ion}'\psi_1]/\gamma_{ion}, \qquad (17)$$

when it follows from Eqns. (15) and (17) that I_{eff} and R diminish with increase of ψ. It can be readily shown that I_{eff} depends on $\beta_A^0 = c_A^0/(c_A^0 + c_B^0)$. Indeed, if the overall concentration of monomers A and B is constant, i.e. $c_A^0 + c_B^0 =$ const., then

$$\frac{I_{eff}(\psi_1)}{I_{eff}(\psi_2)} = \frac{\beta_A(1)}{\beta_A(2)} \simeq \frac{c_A(1)}{c_A(2)}.$$

Thus the copolymerisation of ionogenic monomers is not isoionic for two reasons: (1) a change in β_A^0 automatically leads to a change in the ionic strength (for $c_A^0 + c_B^0$ = const., the increase of β_A^0 entails an increase of I_{eff}, while its decrease reduces I_{eff}); (2) the increase of ψ (for fixed values of β_A^0) is accompanied by a decrease of I_{eff}.

The very fact that I_{eff} changes implies that the propagation rate constants $k_{A(A)}$ and $k_{B(A)}$ are in essence variable quantities. This follows immediately from the analysis of the expression for the rate constants for the interaction between charged species[82,83]:

$$\lg k = \lg k_0 + q_D q_C I_{eff}^{1/2} + (b_D - b_C - b^+) I_{eff}, \tag{18}$$

where k_0 is the reaction rate constant in the absence of low-molecular-weight salts, q_D, and q_C are the charges of the corresponding species D and C, and b_D, b_C, and b^+ are the empirical constants for the D and C species and the activated complex DC.

It is seen from Eqn. (18) than an increase of I_{eff} leads either to an increase (when the charges of the D and C species are of the same sign) or to a decrease (when the charges are of different sign) of the rate constant k.[84] Since the charges of the macroradical and the ionised monomer A are always of the same sign for the instance of copolymerisation in which we are interested, one may expect an increase of $k_{A(A)}$ and $k_{B(A)}$ with increase of I_{eff} [or β_A^0 in the case where $c_A^0 + c_B^0$ = const.]. Since $k_{A(A)}$ and $k_{B(A)}$ are not constants, it follows that the copolymerisation of the ionogenic monomers cannot be described in terms of the two constants r_A and r_B.

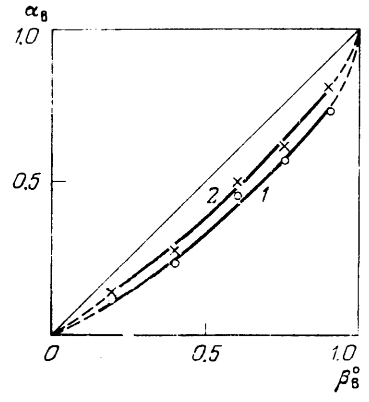

Figure 8. Composition diagram for the acrylamide–potassium *N*-vinylsuccinamate system[95]; concentration of aqueous solution (%): 1) 2; 2) 15.

These considerations have been confirmed experimentally[64,85-90] in relation to a whole series of systems (acrylamide–maleic acid[88], acrylamide–sodium maleate[89], and, in aqueous methanol solutions, acrylonitrile–3-methyl-*N*-vinylimidazolium methyl sulphate[90], acrylamide–sodium fumarate[42], etc.). Somewhat later, interesting results were obtained in a study[91] where the dependence of the composition and the chemical structure of the macromolecules of the copolymers of acrylamide with the lithium, sodium, and potassium salts of acrylic acid on the nature of the counterion was determined (naturally, the comparative analysis was carried out for fixed values of β_A^0 and ψ). When an external electrolyte (NaCl) was introduced into the acrylamide–sodium maleate[92] and acrylamide–sodium fumarate[64] copolymeric systems, the kinetic copolymerisation parameters, the average composition of the macromolecules formed, and the inhomogeneity with respect to composition changed. The last factor can be most simply detected from the change in the parameter

$$y_1 = \{(\bar{\alpha}_A)_z - (\bar{\alpha}_A)_b\}\,(\bar{\alpha}_A)_b = \\ = \left(\sum_{i=1}^{k} w_i \alpha_{Ai}^2 \Big/ \sum_{i=1}^{k} w_i \alpha_{Ai} - \sum_{i=1}^{k} w_i \alpha_{Ai}\right) \sum_{i=1}^{k} w_i \alpha_{Ai} \tag{19}$$

after the introduction of NaCl into the system (for fixed values of β_A^0 and ψ). Here $(\bar{\alpha}_A)_z$ and $(\bar{\alpha}_A)_b$ are respectively the z-average and weight-average compositions of the copolymer; the averaging is carried out with respect to component A. The decrease of y_1 after the addition of NaCl for all values of β_A^0 indicates simpler relations in the synthesis when the process is virtually isoionic[41,93,94] compared with non-isoionic synthesis, so that the inhomogeneity with respect to composition in a non-isoionic process is significantly greater than in an isoionic process.

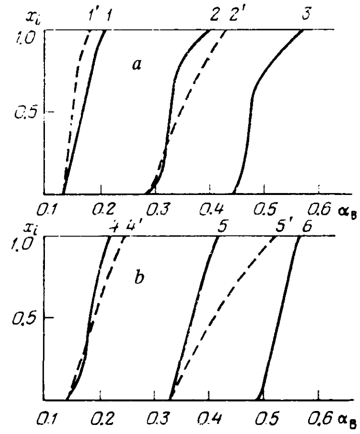

Figure 9. Integral acrylamide–potassium *N*-vinylsuccinamate distribution curves with respect to composition for 2% (*a*) and 15% (*b*) aqueous solutions[95]; β_B^0: 1) and 4) 0.2; 2) and 5) 0.4; 3) and 6) 0.6; ψ: 1) 0.45; 2) 0.76; 3) 0.41; 4) 0.72; 5) 0.73; 6) 0.57; derivative IDCC are shown by dashed lines.

The effect of concentration in the copolymerisation of acrylamide with potassium *N*-vinylsuccinamate has been demonstrated[95]: the composition of the resulting macromolecules depends not only on β_A^0 but also on the overall monomer concentration (Fig. 8). This effect does not occur in classical copolymerisation and is wholly caused by the presence in the system of the ionised monomer, i.e. potassium *N*-vinylsuccinamate. More important information compared with the data derived from the composition diagram (Fig. 8) may be obtained by analysing the experimental IDCC. Fig. 9 shows that the IDCC for statistical copolymers synthesised in 2 and 15% aqueous solutions differ appreciably, namely the IDCC for the 15% solutions are displaced to the right compared with the corresponding IDCC for the 2% solutions. Hence it follows that, on passing from the 2% to the 15% solutions, the relative activity of the salt component in the copolymerisation increases. The failure of the system to obey classical relations is also indicated by the lack of correspondence between the experimental IDCC and their derivatives[43]. The basic IDCC curves from which the derivatives (shown dashed) were obtained were curve *2* for *1*, curve *3* for *2*, curve *5* for *4*, and curve *6* for *5*. An additional illustration of the non-classical nature of the copolymerisation process in the acrylamide–potassium *N*-vinylsuccinamate system may be provided also by the data in Fig. 10, which were obtained by the appropriate treatment[43] of the experimental IDCC in Fig. 9. The form of the relations between $[\beta_B/(1-\beta_B)][g-(1-\alpha_B)/\alpha_B]$ and $\beta_B^2(1-\alpha_B)/(1-\beta_B)^2\alpha_B$ permits the conclusion that the parameters of the interaction of the ionised monomer and the macroradical containing the ionogenic unit not only at the end of the chain but also at a considerable distance from the latter are variable. Fig. 11 demonstrates the difference between the effective[13] sizes of the macromolecular copolymer coils in media where the copolymerisation in 2 and 15% solutions is simulated.

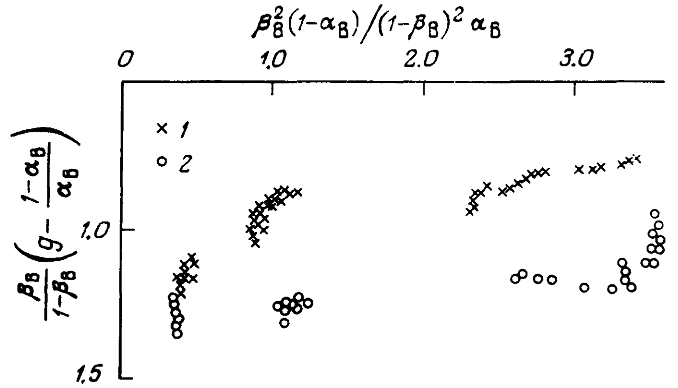

Figure 10. Dependence of $[\beta_B/(1-\beta_B)][g-(1-\alpha_B)/\alpha_B]$ on $\beta_B^2(1-\alpha_B)/(1-\beta_B)^2\alpha_B$ for the acrylamide–potassium vinylamidosuccinate system[95]; concentration of aqueous solution (%): 1) 15; 2) 2.

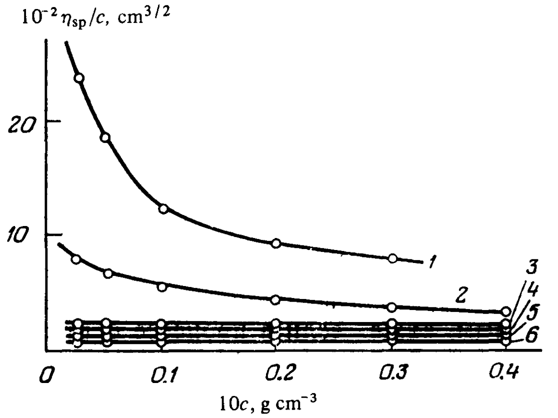

Figure 11. Dependence of the viscosity numbers on concentration for fractions of the acrylamide–potassium vinylamidosuccinate copolymer[95]; $\bar{\alpha}_B = 0.17$ and $\beta_B^0 = 0.2$ for 2% solutions (curves *1*, *3*, and *5*) and $\bar{\alpha}_B = 0.516$ and $\beta_B^0 = 0.6$ for 15% solutions (curves *2*, *4*, and *6*): 1) and 2) in pure water; 3)–6) in the presence of added ionogenic monomer [amount of added ionogenic monomer (%): 3) 0.33; 4) 2.93; 5) 1; 6) 8.8]; η_{sp} = specific viscosity of the solution.

Many of the most important parameters (in the first place the degree of ionisation, the potential of the intramacromolecular interactions between the ionised units, and the conformational parameters of the macromolecules) for polyelectrolytes may be altered by passing from aqueous media to water–organic component mixed solvents[10, 96–98]. Naturally in the copolymerisation process the use of mixed solvents makes it possible to vary within wide limits the rates of the individual reaction stages [mainly $k_{A(A)}$ and $k_{B(A)}$]. It has been shown[99] in relation to the copolymerisation of maleic acid with acrylamide in aqueous dioxan mixtures that, by changing φ (the weight concentration of water in the binary solvent), it is possible to alter specifically the degree of ionisation of the ionogenic units and hence also I_{eff}. It is interesting to note that both in water and in dioxan the copolymerisation is of an unusual type: in water because the process in non-isoionic and in dioxan because the synthesis is a two-phase process[99]. In both instances the experimental IDCC are found to be "anomalously" diffuse. With decrease of φ, the IDCC are shifted to the right (i.e. α_A increases), which may be attributed to the decrease of the effective ionisation constant of maleic acid with increase of dioxan concentration in the binary water–dioxan mixture. The considerable diminution of the anomalous features of the copolymerisation process over a certain range of values of φ merits particular attention. It is associated with two factors: the decrease of the role of polyelectrolyte interactions on passing from purely aqueous to mixed water–dioxan solutions and the fact that the process takes place in a single phase (φ is not sufficiently small to cause the separation of the system into two phases).

(6) An interesting case of "unusual" copolymerisation of the first kind was examined in a study[100] of the copolymerisation of styrene with methacrylic acid (MAA). The "unusual" nature of the copolymerisation was a consequence in the presence in the substrate of the dimeric and non-dimeric forms of the acid. Naturally the relative reactivities of these two forms of methacrylic acid in copolymerisation are different, so that the changes in β_A^0 and ψ automatically entail a change in the relative reactivity of one of the copolymers. The authors confirmed these conclusions by comparing the experimental and blank

(for $r_A = 0.7$ and $r_B = 0.15$) distribution curves with respect to composition.

4. Unusual Systems of the Second Kind ("Anomalous" Systems)

These systems include those where the copolymerisation process is accompanied by such marked deviations from the classical Mayo–Lewis mechanism that the unambiguous relation between β_A and α_A breaks down. This has the automatic consequence that the characteristics of the classical copolymerisation process (or at least the main ones) do not hold for unusual systems of the second kind. Naturally, the correct analysis of "anomalous" systems requires the most complete information possible about the distribution with respect to composition and about the characteristics of the chemical structure of the copolymer macromolecules.

(1) Suppose that the copolymerisation takes place as a heterophase process. It has been shown[8,101] that, depending on the conditions of the synthesis, the resulting distribution with respect to composition is bi- or tri-modal. Naturally, in this instance one cannot always reach the correct conclusion about the conditions under which a particular fraction with the composition α_{Ai} is obtained, even if r_A = const. and r_B = const. in the synthesis. As an example, Fig. 12 presents experimental composition diagrams for copolymers of methyl methacrylate (A) with methacrylic acid; the synthesis was carried out in mixed water–dioxan solvents with variable compositions[102]. In region *LR* (shown schematically by dashed lines) the unambiguous relation between m_A and M_A breaks down. The region *QR* is particularly interesting, because in the latter M_A should increase with increase of ψ, while in the remainder of the composition range M_A decreases with increase of ψ.

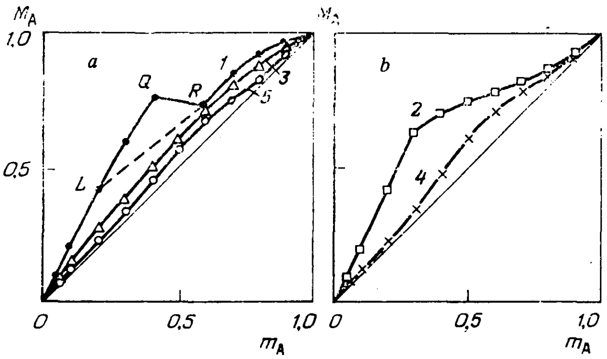

Figure 12. Composition diagrams for methyl methacrylate (A)–methacrylic acid (B) copolymers for different water : dioxan ratios: 1) 100 : 0; 2) 80 : 20; 3) 50 : 50; 4) 30 : 70; 5) 0 : 100.[102]

Consider another system—the copolymerisation of acrylamide (A) with potassium *N*-vinylsuccinamate (B).[103] The greatest amount of information about the process can be obtained by comparing the IDCC found separately for each phase (naturally, one is dealing with a heterophase process). The necessity for the separate comparison of the IDCC for copolymers isolated from phases 1 and 2 arises from the fact that, without preliminary calibration experiments, it is impossible to establish in which particular phase the specific copolymer fractions have been obtained[8]. Fig. 13 presents the IDCC for the A–B copolymers synthesised in binary water–dioxan and water–methanol solvents. We may note that the copolymeric A–B system investigated is "anomalous" not only in consequence of the heterophase nature of the synthesis but also because of the variability of the relative reactivities of monomers A and B in copolymerisation[104].

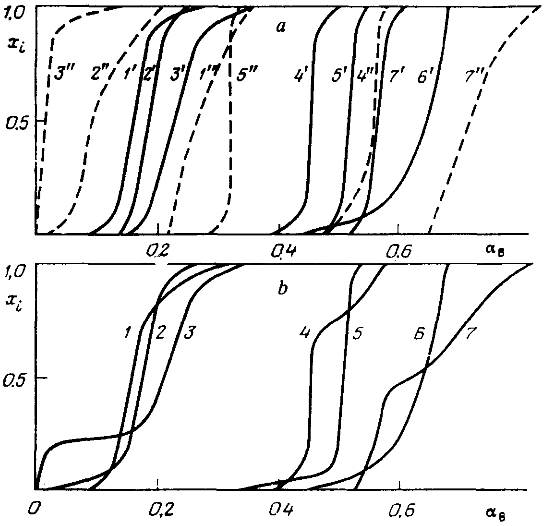

Figure 13. Integral distribution curves with respect to composition for acrylamide–potassium *N*-vinylsuccinamate copolymers[103]: *a*) separately for concentrated and dilute phases; the IDCC for specimens isolated from the dilute phase (curves *1″*–*7″*) are shown by dashed lines, while continuous lines represent the curves for the specimens isolated from the concentrated phase (curves *1′*–*7′*); *b*) overall IDCC for specimens isolated simultaneously from the dilute and concentrated phases (curves *1*–*7*). Reaction medium: 1), 1′), and 1″) water : methanol = 1 : 3; 2), 2′), and 2″) water : dioxan = 1 : 1; 3), 3′) and 3″) water : dioxan = 1 : 2; 4), 4′), 4″), 7), 7′), and 7″) water : methanol = 1 : 5; 5), 5′), 5″), 6), 6′), and 6″) water : dioxan = 1 : 3; β^0_B: 1), 1′), 1″), 2), 2′), 2″), 3) 3′), and 3″) 0.2; 4), 4′), 4″), 5), 5′), 5″) 0.6; 6), 6′), 6″), 7) 7′), and 7″) 0.8.

Labile hydrogen bonds[105] as well as the nature of the heterogeneous equilibrium in the multicomponent system[106,107] can also complicate the copolymerisation process. However, even a qualitative comparison of the IDCC (Fig. 13) permits the important conclusion that, depending on the nature of the precipitant employed, the copolymer in the concentrated phase is enriched (dioxan) or depleted (methanol) in component B relative to the copolymer in the dilute phase. The explanation is that the homopolymer B and copolymers with a high content of B are soluble in methanol, which is a very effective precipitant for polyacrylamide. Dioxan does not behave as a precipitant either for homopolymers or for copolymers of different compositions. After the attainment of a critical degree of conversion ψ_{cr}, the "displacement" of the monomeric component B from the solution to the concentrated phase is much less pronounced than in the water–dioxan system according to the Langmuir rule. Thus in heterophase synthesis a kind of fractionation of the copolymer with respect to composition between dilute and concentrated phases take place already during the formation of macromolecules, the choice of the solvent–precipitant system determining in many respects the properties of the reaction products. In this connection it is appropriate to mention that the IDCC are much more reliable "indicators" of different types of interphase interactions than molecular weight distribution curves.

An interesting case of "anomalous" copolymerisation in a precipitant was examined by Slavnitskaya et al.[108] In conformity with the general mechanism of heterophase copolymerisation[101], the experimental IDCC were trimodal. Comparative analysis of the individual branches of the overall IDCC led Slavnitskaya et al.[108] to important conclusions about the copolymerisation mechanism, particularly about the intensity of the kinetic chain propagation and termination process in individual phases of the system.

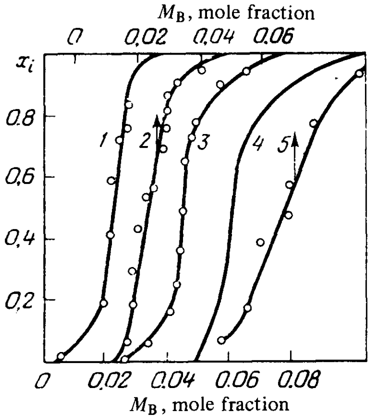

Figure 14. Integral distribution curves with respect to composition for ethylene (A)–triethylvinylsilane (B) copolymers with different average contents $\bar{\alpha}_B$ of component B: 1) 0.018; 2) 0.03; 3) 0.41 (Samoilov et al.[109]); 4) 0.069 (Samoilov et al.[109]); 5) 0.066.

(2) Copolymerisation complicated by intense depolymerisation processes. The breakdown of the unambiguous nature of the relation $\alpha_A = f(\beta_A)$ may be expected when the rate constants for the depolymerisation of the first and second components differ appreciably. This apparently happened in a study[109] of the radical copolymerisation of ethylene with trimethyl- and triethyl-silanes at 160°C and 1400 atm using di-t-butyl peroxide as the initiator. On the basis of the composition diagram and the analysis of the results in terms of the Feinman–Ross coordinates, the authors reached the well argued conclusion that the Mayo–Lewis equation is inapplicable to the system. This is also clearly indicated by data for polydispersity with respect to composition for the same copolymers (Fig. 14). In view of a number of indirect pieces of evidence, the authors[109] fully rule out a heterophase copolymerisation mechanism, but in our view (bearing in mind the form of curves *1*, *2*, and *4* in Fig. 14) the partial heterophase nature of the system may make a definite contribution to the "abnormality" of the system apart from the depolymerisation processes.

The principal characteristics of copolymerisation when polymerisation and depolymerisation processes occur simultaneously was examined in detail in a review[110]. In particular, the review deals with the influence of the ratio of the rate constants for the forward and reverse (depolymerisation) processes on the composition of the macromolecules formed. It is shown that the composition diagrams differ significantly when the relative contribution of the depolymerisation process to the overall copolymerisation reaction balance is varied (Fig. 15), which is achieved most simply by altering the temperature of the copolymerisation process.

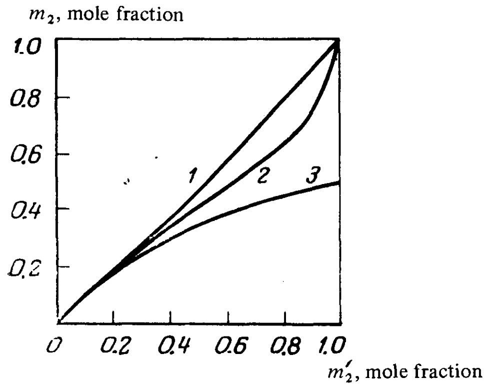

Figure 15. Composition diagrams in the presence of the depolymerisation process at different temperatures (°C): 1) 0; 2) 50; 3) 100; m_2 and m_2' are the mole fractions of the second component in the copolymer and in the mixture of monomers respectively.

(3) The ambiguity of the $\alpha_A = f(\beta_A)$ relation in two-centre copolymerisation was demonstrated experimentally[111] for the copolymerisation of N-butylidenecyclohexylamine with acrylonitrile.

(4) The "anomalous" nature of the system is due to intense reactions involving kinetic chain transfer to macromolecules. Such systems have been examined[112] in relation to the copolymerisation of styrene with dioxolan and elsewhere[113] for the copolymers of oxacyclobutane with β-propiolactone. In the latter study[113] the "anomalous" nature of the copolymer was demonstrated by direct analysis of its chemical structure. The main theoretical principles of copolymerisation complicated by chain transfer reactions with rupture of the macromolecules were formulated by Enikolopov[23]. One should note that, in the polymerisation of cyclic compounds, many parameters of the final product (particularly the nature of the molecular

weight distribution) depend on the degree of departure of the reaction from equilibrium[20,114].

We shall consider in greater detail the copolymerisation of cyclosiloxanes, because, according to literature data[115], intense interchain exchange reactions at the stage of the synthesis are to be expected for polymers of this class. On the other hand, the occurrence of various secondary reactions should affect to the greatest extent the distribution curves with respect to composition. Fig. 16 presents the IDCC for copolymers of dimethyl- and methylphenyl-siloxanes[116] (analogous relations were obtained also for SKTNF rubber[117]). We may not in the first place that, whereas the difference between the compositions of the fractions detected during fractionation without employing selective solvent–precipitant mixtures[5,118–120] exceeds only slightly the limit of the sensitivity of the method (under somewhat different fractionation conditions, no differences between the compositions of the fractions were noted at all in another study[121]), in fractionation employing selective solvent–precipitant systems sensitive to the composition of the macromolecules the difference between the compositions of the isolated fractions greatly exceeds this value. The very difference between the compositions of the fractions (Fig. 16) permits the conclusion that the interchain exchange processes do not suppress completely the main process involving the synthesis of the macromolecules of a copolymer having a definite structure, in conformity with the relative reactivities of the monomers and their concentrations. Indeed if depolymerisation and chain transfer to macromolecules played the main role, one should expect a high degree of homogeneity of the fractions with respect to composition, which conflicts with experimental data in Fig. 16. On the other hand, since $\psi \geqslant 0.9$ for all the specimens, one might expect a greater polydispersity of the fractions with respect to compositions on the assumption that the Mayo–Lewis scheme applies. The conclusion that the scheme does not apply is consistent with those reached by investigators[122] who studied the copolymerisation of octamethyl- and octaphenylcyclotetrasiloxanes.

The following most probable chain transfer reactions may be considered[114,115]:

$$\sim R_1R_2SiO^- + \sim SiR_1R_2OSiR_1'R_2' \sim \xrightarrow{k_1'} \sim R_1R_2SiOSiR_1R_2 \sim + \sim R_1'R_2'SiO^-,$$

$$\sim R_1R_2SiO^- + \sim SiR_1'R_2'OSiR_1'R_2' \sim \xrightarrow{k_2'} \sim R_1R_2SiOSiR_1'R_2' \sim + \sim R_1'R_2'SiO^-,$$

$$\sim R_1'R_2'SiO^- + \sim SiR_1'R_2'OSiR_1R_2 \sim \xrightarrow{k_3'} \sim R_1R_2SiO^- + \sim R_1'R_2'SiOSiR_1'R_2' \sim,$$

$$\sim R_1'R_2'SiO^- + \sim R_1R_2SiOSiR_1R_2 \sim \xrightarrow{k_4'} \sim R_1'R_2'SiOSiR_1R_2 \sim + \sim R_1R_2SiO^- . \tag{20}$$

The fact that for certain compositions of the initial mixture of cyclosiloxanes the copolymerisation cannot be regarded *a priori* as a homophase process after the attainment of ψ_{cr} may also have a significant influence on the copolymerisation reaction, particularly on the distribution curves with respect to composition[122]. The lack of information about the relative reactivities of different cyclic monomers in the copolymerisation reaction[123] and about the composition of the mixture of monomers during the synthesis precludes a quantitative assessment of the degree of departure from equilibrium and of the role of the chain transfer reactions in the copolymerisation. However, the results already obtained do indicate the necessity for careful studies on these lines with the obligatory involvement of data for the distribution of copolymers with respect to composition.

Naturally, the "anomalous" nature of the system persists also when the principal necessary conditions for the classification of the process break down simultaneously (for example, when depolymerisation accompanies the process under heterophase conditions, when reactions involving chain transfer to the polymer are accompanied by two-centre copolymerisation, etc.). It is quite unreasonable to use the copolymerisation "constants" r_A and r_B for all "anomalous" systems. For such systems, even the available information about the distribution with respect to composition within the specimen for different values of β_A^0 and ψ is insufficient in certain instances for the estimation of the characteristic features of the copolymerisation process and it is necessary to resort to data for the real chemical structure of the macromolecules (for example, in heterophase copolymerisation with intense interphase recombination interactions or in the presence of intense kinetic chain transfer reactions between the phases, etc.).

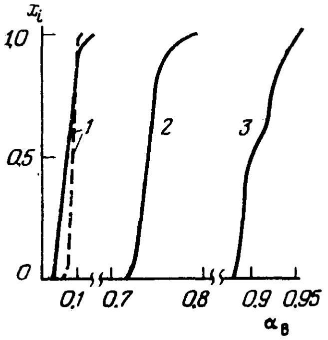

Figure 16. Integral distribution curves with respect to composition for SKDFV-803 (curves *1* and *2*) based on fractional dissolution (curve *1*) and fractional precipitation (curve *2*) data for copolymers of methylphenyl- and dimethyl-siloxanes with ratios of the initial monomers of 3 : 2 (curve *2*) and 4 : 1 (curve *3*).[116]

IV. METHODOLOGICAL RECOMMENDATIONS

Thus binary statistical copolymerisation may be classical, classical in a certain range of β_A^0 and ψ, and unusual (of the first and second kind). However, the answer to the question whether a specific process is classical or unusual is far from trivial. The point is that it is extremely difficult to state *a priori* whether a particular condition necessary for a classical process holds; on the other hand, successive tests of the validity of all twelve conditions formulated above are too cumbersome. For this reason, a simpler analytical scheme is necessary in which a conclusion concerning the topology of the copolymerisation process is reached on the basis of a comparison of the individual features of the specific copolymerisation system and a classical system.

In this sense the following analytical procedure is most promising. In the first stage one analyses the $\alpha_A = f(\beta_A^0)$ relation and, when the latter is not unambiguous, the system is known to be "anomalous" (unusual system of the first kind). For such systems, it is erroneous to calculate the apparent copolymerisation "constants" [obtained by the formal treatment of the $\alpha_A = f(\beta_A^0)$ relations]: it is necessary to analyse the IDCC and the chemical structure of the specimens for different β_A^0 and ψ. When the $\alpha_A = f(\beta_A^0)$ relation is ambiguous, it is necessary to determine whether it can be described in terms of two copolymerisation constants ($r_A \pm \Delta r_A$ and $r_B \pm \Delta r_B$) or whether the function $\alpha_A = f(\beta_A)$ is more complex. Several approaches are possible in order to obtain an answer to the last question.

The first involves the comparative analysis of the experimental values $(\Delta r_A/r_A)_{exp}$ and $(\Delta r_B/r_B)_{exp}$ together with the calculated values $(\Delta r_A/r_A)_{calc}$ and $(\Delta r_B/r_B)_{calc}$. If $(\Delta r_A/r_A)_{exp} \gg (\Delta r_A/r_A)_{calc}$ and $(\Delta r_B/r_B)_{exp} \gg (\Delta r_B/r_B)_{calc}$, then unusual copolymerisation is indicated[19,26].

In the second procedure the formal values of r_A and r_B may be used to plot theoretical IDCC[124,125] which are then compared with the experimental curves. The conclusion whether or not the process is unusual or classical can be reached on the basis of the positions, widths, and shapes of the experimental and theoretical IDCC.[4,26]

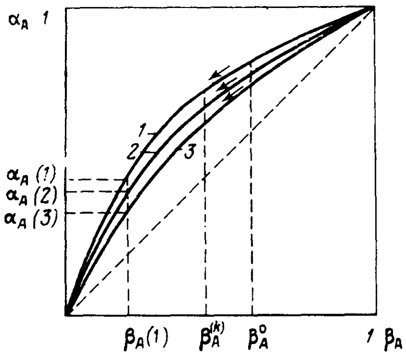

Figure 17. Schematic composition diagrams for different ψ = const.: 1) ψ_1; 2) ψ_2; 3) ψ_3; $\psi_1 < \psi_2 < \psi_3$.

In the third procedure conclusions are reached about the unusual or classical nature of the process from a comparison with experimental curves of the theoretical IDCC plotted on the basis of data derived from the composition diagram (without calculating r_A and r_B). We shall consider in greater detail the plotting of theoretical IDCC by this method, because it is extremely important from the practical point of view. Suppose that we do not know the form of the $\alpha_A = f(\beta_A)$ function and have at our disposal only empirical data of the type of composition diagrams. Suppose further that $\alpha_A < \beta_A$, which means that α_A increases with increase of ψ (Fig. 17). If

$$\beta_A|_{\psi=0} = \beta_A^0 = c_A|_{\psi=0}/(c_A|_{\psi=0} + c_B|_{\psi=0}) \text{ and}$$
$$\beta_A^{(k)} = \beta_A|_{\psi=\psi_k} = c_A|_{\psi=\psi_k}/(c_A|_{\psi=\psi_k} + c_B|_{\psi=\psi_k});$$
$$c_A|_{\psi=0} + c_B|_{\psi=0} - c_B|_{\psi=\psi_k} - c_B|_{\psi=\psi_k} = \Delta c_A + \Delta c_B;$$

then the average weight content of component A in the copolymer is

$$\bar{\alpha}_A = \Delta c_A|_{\psi=\psi_k}/(\Delta c_A|_{\psi=\psi_k} + \Delta c_B|_{\psi=\psi_k}),$$

and

$$\psi_k = (\Delta c_A + \Delta c_B)/(c_A + c_B)|_{\psi=0} .$$

Without infringing the generality of the approach, we put $(c_A + c_B)|_{\psi=0} = 1$. In order to plot the weight IDCC, the entire $\Delta c_A = |c_A|_{\psi=\psi_k} - c_A|_{\psi=0}|$ section must be divided into a polymerisation increments[22] (smooth relations between $\psi^{(i)}$ and $\alpha_A^{(i)}$, which are necessary for accurate IDCC plots, can be achieved when $a \simeq 20$). For the first polymerisation increment, we have

$$\beta^1_{(A)} = \frac{\beta_A|_{\psi=0} - \Delta c_A/a}{1-\psi^{(1)}};\ \bar{\alpha}_A^{(1)} = \frac{\Delta c_{A/a}}{\Delta c_A/a + \Delta c_B^{(1)}} = \frac{\Delta c_A}{a\psi^{(1)}};$$
$$\beta_A^{(1)}(1-\psi^{(1)}) = \beta_A|_{\psi=0} - \bar{\alpha}_A^{(1)}\psi^{(1)}.$$

Hence $\psi^{(1)} = \Delta c_A/a + \Delta c_B^{(1)} = (\beta_A^{(1)} - \beta_A^0)/(\beta_A^{(1)} - \bar{\alpha}_A^{(1)})$. $\psi^{(2)}, \psi^{(3)}, \ldots$ can be calculated similarly, but one must recall that a proportion of the monomers are consumed in preceding polymerisation increments, so that

$$\psi^{(2)} = \frac{\beta_A^{(2)} - \beta_A^{(1)}}{\beta_A^{(2)} - \bar{\alpha}_A^{(2)}}[1-\psi^{(1)}];\ \psi^{(3)} = \frac{\beta_A^{(3)} - \beta_A^{(2)}}{\beta_A^3 - \bar{\alpha}_A^{(3)}}[1-\psi^{(1)}][1-\psi^{(2)}],$$

etc. After calculating all the $\psi^{(p)}$ for $p \leqslant a$, it is easy to convert the result into the integral weight fraction of the increment and then plot the weight IDCC. Similarly it is not difficult to calculate the molar IDCC; in this case one must employ a molar composition diagram. Conclusions whether or not the copolymerisation process is unusual or classical can also be reached by other indirect methods. Some of these are indicated below.

(1) Suppose that the copolymerisation process takes place in a solvent. For a classical process, α_A is determined by the values of $\bar{\beta}_A$ and ψ and is independent of the overall monomer concentration ($c_A^0 + c_B^0$). The appearance of a dependence of α_A on $c_A^0 + c_B^0$ shows unambiguously that the process is unusual. We examined this case in detail previously in relation to the copolymerisation of ionogenic monomers in ionising media.

(2) The study of the distribution with respect to composition for $\beta_A = (\beta_A)_{az}$. For classical systems, the specimen should be monodisperse and the parameter y_1 [see Eqn. (19)] should be zero also when $\psi \to 1$ (it is assumed that the degree of polymerisation is fairly high and that the "instantaneous" component of the inhomogeneity with respect to composition may be neglected). On the other hand, if y_1 differs appreciably from zero to $\beta_A = (\beta_A)_{az}$, the implication is that the copolymerisation process has an unusual mechanism. In this case unusual distribution curves with respect to composition may be expected for specimens obtained by heterophase copolymerisation—one branch of the curve should be convex and the other should be concave with respect to the abscissa axis.

(3) In many instances the conclusion that the nature of the copolymerisation process is unusual may be arrived at by comparing the values of y_1 for model and experimental IDCC.[36,43]

It is necessary to note yet another important factor—the points on the composition diagrams must be analysed for the same values of ψ. As shown schematically in Fig. 17, the values of α_A for the same β_A may differ appreciably for different ψ. The analysis where values of α_A are determined as a function of ψ for different β_A^0 and the results are used to find $\bar{\alpha}_A$ for the required values of $\psi = \psi_A$ is most suitable for a practical study. If ψ varies within wide limits under these conditions, then the above type of analysis yields an amount of information intermediate between that derivable from the analysis of the IDCC and the analysis of the composition diagrams.

In conclusion of this section, a few words must be said about the Alfrey–Price $Q-e$ scheme[126,127]. In the first place one must understand that the scheme is in principle applicable solely to the analysis of classical systems. The Alfrey–Price scheme is empirical and can be useful only in a comparative analysis of the binary statistical copolymerisation of A and B, A and B′, A and B″, etc. monomers, where B, B′, B″, ... are vinyl monomers differing in the group R, but the copolymerisation conditions must be identical. It is illegitimate to apply the Alfrey–Price scheme to the estimation of the reactivities of 1,1- and 1,2-disubstituted ethylenes, because the scheme does not take into account the role of the steric factor[128,129]. The difficulties arising in the application of the Alfrey–Price scheme are hardly resolvable if the relative reactivities of the monomers depend on the parameters of the reaction medium. Indeed, in this case Q_A, Q_B, e_A, and e_B cease to be unambiguous and the Alfrey–Price scheme itself becomes arbitrary. The attempt to employ the Alfrey–Price scheme in the analysis of systems where for even one of the monomer pairs [part of the Russian text appears to be missing at this point] (the copolymerisation is an unusual process of the first or second kind) is known *a priori* to be unsatisfactory. We have to consider these self-evident matters because many workers, while realising the limited nature of the Alfrey–Price scheme, contradict themselves by employing it.

The question of the much greater complexity of the characteristics of the copolymerisation of a large class of systems compared with the characteristics of the copolymerisation of classical systems is no longer controversial. Naturally, the increase in the complexity of the copolymerisation mechanism requires the formulation of more complicated experiments and a more complicated method of interpretation of the experimental data[130] (compared with classical systems). The employment of data for distribution with respect to composition[131] and also the derivation of information about the chemical structure (configurational inhomogeneity) or macromolecules are not only desirable but also necessary[8,10]. This review deals only with the principal criteria for the estimation of the characteristics of binary statistical copolymerisation and the most general copolymerisation model has been adopted for the treatment. The general principles described are illustrated by the analysis of the characteristics of copolymerisation for a number of specific models.

Further progress in the development of a general statistical copolymerisation theory will be evidently associated with an intense development of research on the following lines: (1) the discovery and development of new reliable methods for the determination of the statistical parameters of copolymerisation, in the first place the IDCC and the chemical structure of the macromolecules. Together with the high-resolution NMR method[132], the degradation method[133] is in many cases promising for the estimation of structure. The degradation method is particularly effective in the absence of a depolymerisation process and for a sharp difference between the degradation rate constants k_g for components A and B. In particular, analysis of the molecular weight distribution (MWD) curves for degradation products permits important inferences about the characteristic features of the synthesis of copolymers. Thus unimodal and bimodal MWD curves for the products of the ozonolysis of statistical copolymers of isobutene (A) and butadiene (B) $[k_g(A) \ll k_g(B)]$ indicate homophase[134] and heterophase[135] synthesis of copolymers. The determination of quantitative relations between MWD and the Schultz parameters for the degradation products, on the one hand, and the IDCC and the parameters of dispersion with respect to the composition of the copolymer, on the other, appears quite realistic; (2) the accumulation of experimental data on the characteristics of the copolymerisation of unusual systems; (3) the development of theories which establish a relation between the statistical parameters and the process mechanisms for specific unusual (of the first and second kind) copolymerisation models[136]; (4) the development of the most complete classification scheme for the analysis of binary statistical copolymerisation based on a general copolymerisation model.

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Thin-layer Chromatography of Polymers

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A new method for the investigation of the polydispersity of polymers in terms of molecular weight, composition, regularity, and stereoregularity—the thin-layer chromatography of polymers—is described. The theoretical principles of the method, quantitative analysis, and its application to the study of various classes of polymers and oligomers are considered. The bibliography includes 102 references.

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I. INTRODUCTION

A major advance in the development of thin-layer chromatography (TLC) has been its application to the analysis of high polymers. The first studies on the TLC of statistical copolymers were carried out in 1968 simultaneously at the Analytical Laboratory of the Institute of Macromolecular Compounds of the USSR Academy of Sciences[1] and in Inagaki's laboratory at Kyoto University[2]. Since then the following principal trends have been established in this new field of chromatography[3-6]: the study of the heterogeneity of polymers [molecular weight distribution (MWD) and inhomogeneity with respect to composition]; identification (diagnosis) of polymers differing in microstructure; analysis of MWD and the functionality of oligomers.

Depending on the nature of the interactions in chromatographic systems, the following types of TLC of polymers are possible: (a) adsorption TLC of polymers (ATLC) in which differences in the adsorption activity of polymers are used, the differences increasing with increase of the molecular weight (MW) and the fraction of adsorption-active polar groups in the copolymer or oligomer; (b) thin-layer gel-permeation chromatography (TLGPC) based on the use of the molecular sieve effect, in which the separation of polymers is associated with the differences between the relative dimensions of the macromolecule and the dimensions of the pores in the adsorbent; (c) precipitation TLC of polymers (PTLC) based on differences between the solubilities of polymers having different molecular weights and different chemical structures; (d) extraction TLC (ETLC), in which polymers of different types are selectively dissolved in the initial spot on the "all or nothing" principle. These versions of the TLC of polymers can be usefully combined into two groups, differing in the mechanism of the fractionation of macromolecules: (1) adsorption methods (ATLC) with positive adsorption and TLGPC with negative adsorption; (2) methods based on differences between the solubilities of polymers (PTLC and ETLC).

At the present time TLC is used widely in the study of high-molecular-weight substances. Here one may point out that TLC is used successfully in the quantitative analysis of polymers: for the analysis of the molecular weight distribution (MWD) of homopolymers (ATLC, PTLC), statistical copolymers (PTLC), and oligomers (ATLC), the inhomogeneity of block and statistical copolymers with respect to composition (ATLC), the functionality of oligomers (ATLC), and the functionality of polymers (with $M < 5 \times 10^4$) having terminal adsorption-active groups (ATLC, ETLC). TLC is also employed for the quantitative analysis (diagnosis) of the branching of homopolymers and oligomers (ATLC) and the microstructure of polymers: the regularity of polybutadiene and polyisoprene (ATLC, ETLC), the stereoregularity of poly(methyl methacrylate) and polystyrene (ATLC, PTLC, ETLC), statistical, alternating, and block copolymers (ATLC) and two- and three-block copolymers (ATLC), and the analysis of the purity and homogeneity of polymer fractions, the admixture of homopolymers in block and graft copolymers (ATLC, PTLC, ETLC), and the side chains split off from graft copolymers and the corresponding homopolymers (ATLC). TLC is also used in combination with other chromatographic techniques [gel permeation (GPC) and pyrolytic gas chromatography (PGC)] in the analysis of complex polymer systems where the problems enumerated above are solved with the aid of TLC.

II. THIN-LAYER CHROMATOGRAPHY OF POLYMERS BASED ON ADSORPTION

1. Adsorption TLC (ATLC) of Copolymers

ATLC was the first version of the TLC of polymers developed by ourselves[1,7-9] and Inagaki[2] for the fractionation of statistical ST–MMA and ST–MA copolymers† with respect to composition. Eluent systems consisting of chlorinated hydrocarbons and solvents and adsorption-active oxygen compounds as displacing agents were used for the TLC of ST–MMA copolymers; they can be arranged in the following eluotropic series: ethyl ether < EMK < acetone < THF < dioxan; chlorobenzene < dichloroethane < chloroform. The copolymers were chromatographed in sandwich chambers (S-chambers), where a concentration gradient of the displacing agent was set up by its gradual evaporation into the air space within the chamber while flowing along the plate. High gradients were used to separate copolymers with large differences in composition (Fig. 1‡). ST and MMA copolymers, the elemental compositions of which are virtually indistinguishable, can be fractionated by high-resolution TLC with a weak displacing agent concentration gradient; for example, it is possible to observe differences in the polydispersity of copolymers having an azeotropic composition (with 54 mole % ST), obtained for different conversions. It was observed[3,7] that the R_f (relative migration) of the copolymer depends not only on the composition, but also on its molecular weight (for MW < 10^5). Similar results for the TLC of ST–MA statistical polymers were obtained in a study[2] where gradient TLX was used with addition of methyl and ethyl acetates to chloroform.

The distribution and inhomogeneity with respect to composition of many other statistical copolymers (styrene–butadiene, styrene–acrylonitrile, incompletely substituted cellulose nitrates and acetates, and α-amino-acid copolymers) were investigated with the aid of ATLC—see Appendix (Table 1).

Inagaki established[10] that the chromatographic mobility of ST–MMA copolymers is related to their structure. Thus the R_f for these copolymers in the chloroform–ethyl acetate system increase in the following sequence: block copolymers < alternating copolymers < statistical copolymers; the values of R_f for block copolymers vary as a function of the number of blocks incorporated in them[11,12].

2. ATLC of Homopolymers

The considerable possibilities of ATLC for the separation of homopolymers on the basis of their molecular weights have been demonstrated[13]. Fig. 2 illustrates chromatograms for narrowly disperse polystyrenes ($M_w/M_n \leqslant 1.2$) on KSK silica gel plates in the cyclohexane–benzene–acetone system.

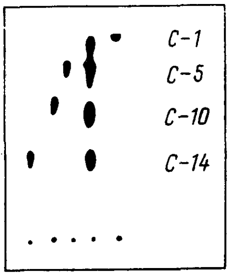

Figure 1. TLC of statistical ST–MMA copolymers on KSK silica gel in the 12 : 2.2 chloroform + acetone system in an S-chamber: C-14 (22% ST, $M_w = 2.3 \times 10^5$); C-10 (31% ST, $M_w = 8.8 \times 10^4$); C-5 (54% ST, $M_w = 8 \times 10^4$); C-1 (80% ST, $M_w = 1.2 \times 10^5$).

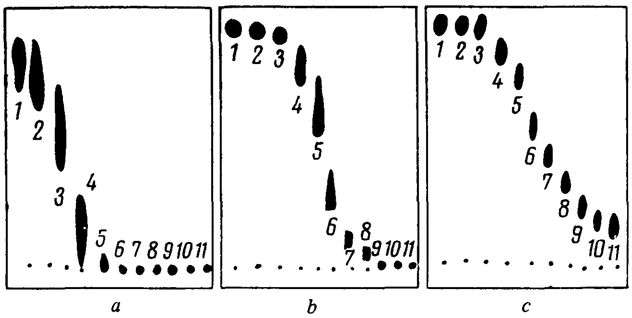

Figure 2. TLC of polystyrenes ($M_w/M_n \leqslant 1.2$) on KSK silica gel in the cyclohexane + benzene + acetone system: *a*) 13 : 3 : 1; *b*) 12 : 4 : 0.4; *c*) 12 : 4 : 0.7; 1) $M_n = 10^3 \times 0.9$; 2) $M_n = 10^3 \times 2.03$; M_w/M_n; 3) 5/4.5; 4) 10.3/9; 5) 19.85/19.65; 6) 51/49; 7) 98.2/96.2; 8) 173/164; 9) 411/392; 10) 867/773; 11) 2145/1780.

If solvents with relatively low adsorption activity, for example, a mixture of cyclohexane and benzene, are used for the ATLC of polystyrene, then polystyrenes with MW > 10^5 do not form compact spots and are smeared over the plate, which is due to the low rate of the adsorption-desorption processes involving high-molecular-weight polymers in such systems.

It has also been possible to resolve PMMA by adsorption TLC in the 5 : 95 methanol–chloroform system[14,15] and PEO in the ethylene glycol–methanol system on silica gel and the methanol–DMF system on alumina on the basis of their molecular weights[16].

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†The following abbreviations have been adopted in this review: ST = styrene, PS = polystyrene, MMA = methyl methacrylate, MA = methyl acrylate, PMMA = poly(methyl methacrylate), EO = ethylene oxide (epoxyethane], PEO = poly(ethylene oxide), PB = polybutadiene, BD = butadiene, P-α-methylstyrene, AN = acrylonitrile, PI = polyisoprene, CTA = cellulose triacetate, PVA = poly(vinyl acetate), ETP = ethylene terephthalate, PETP = poly(ethylene terephthalate), PPG = poly(propylene glycol), EMK = ethyl methyl ketone, THF = tetrahydrofuran, and DMF = dimethylformamide.

‡Fig. 1 and other figures represent contact photographs of thin-layer chromatograms.

3. Thin-Layer Gel-Permeation Chromatography of Polymers (TLGPC)

The possibility of separating polymers with the aid of TLC on the basis of the molecular sieve mechanism was first established by Halpaap and Klatyk[17], and the feasibility of its application to the analysis of TLGPC was first studied by Belenkii et al.[3] This form of TLC of polymers has also been studied in other investigations[18,19]. In order to reveal the molecular-sieve effect in TLC, it is necessary to suppress the adsorption activity of silica gel and to fill the adsorbent pores with the solvent before the start of elution. This can be achieved in two ways: with the aid of so-called pre-elution, i.e, by passing the solvent along the plate before depositing the sample[18], or by capillary condensation involving the preliminary saturation of the chromatographic layer on the plate with solvent vapour[3,13]. It has been shown[18] that the effectiveness of TLGPC in the separation of polymers on the basis of their molecular weights depends on the degree of saturation with the solvent of the adsorbent pores and of the space between the particles of the chromatographic layer. This is the reason for the differences in the effectiveness of TLGPC as a function of the thickness of the adsorbent layer and the direction of motion of the eluent (upwards or downwards) along the plate. For this reason, column GPC is more effective than TLGPC, where the packing density of the adsorbent is lower.

4. Fundamental Characteristics of Adsorption TLC Methods for Polymers (ATLC and TLGPC)

The adsorption of polymers has been studied in many theoretical and experimental investigations[20]. The most notable achievement in this field has been the prediction[21-24] of the phase transition occurring after the attainment of a critical value ϵ_{cr} in the energy of the interaction of the polymer unit with the adsorption surface (ϵ). In this transition all the properties of the adsorbed macromolecule change: its size, the fraction of adsorbed segments, and the sign of the free energy change (there is a transition from negative to positive adsorption), i.e. $-\Delta F = 0$ when $-\epsilon = -\epsilon_{cr}$. It has been shown theoretically[24] that these features are characteristic of the adsorption of isolated macromolecules both on a planar surface and within pores.

The chromatographic experiments made it possible to investigate the adsorption behaviour of macromolecules in the absence of concentration effects, i.e. one can study experimentally the behaviour of isolated macromolecules. These features of the adsorption behaviour of macromolecules have been tested experimentally[25] by TLC on silica gels in the hydrogen-form ensuring the energetic equivalence of the surfaces of silica gel adsorbents of different porosities[26]. Narrowly disperse PS were chromatographed in the 40 : 16 : x cyclohexane–benzene–acetone system, where changes in the acetone content (x) regulated the energy of the interaction ($-\epsilon$) of the macromolecular segment with the adsorbent surface. The quantity $-\epsilon$ (in units of kT) can be expressed in the form $-\epsilon = \epsilon_{pa} - \epsilon_{sa}$, i.e. as the difference between the energies of the adsorption interactions of the polymer segment (ϵ_p) and the solvent (ϵ_{sa}). Since ϵ_p remains constant when the solvent composition is altered, ϵ is determined in terms of the quantity ϵ_s, which may be calculated by Snyder's method[27].

Fig. 3 presents PS chromatograms on KSK silica gel (pore diameter 100 Å).[25] Evidently, with increase of the acetone content and hence with decrease of $-\epsilon$, there is a gradual transition from adsorption to molecular sieve chromatography. The chromatograms illustrated in Fig. 3 have the following features: (1) with increase of $-\epsilon$ (i.e. with increase of x) in the region of the preferential operation of the molecular sieve effect (MSE), where negative adsorption is observed (Figs. 3*d*–3*f*), the R_f for the large PS macromolecules diminish; the macromolecules are, as it were, "drawn into" previously inaccessible pores, i.e. the limit corresponding to the exclusion of macromolecules from the pore space is determined not only by the MSE (the ratio of the dimensions of the macromolecules and pores) but also by the adsorption in the pores; (2) there exists a composition of the eluent for which the energy of the interaction of the molecular segments with silica gel is close to the critical value $-\epsilon_{cr}$ (Fig. 3*c*); PS molecules with different molecular weights then exhibit identical values of K_d and R_f and the macromolecules are, as it were, insensitive to the pore dimensions (zero adsorption); (3) on further decrease of x (on increase of $-\epsilon$), there is a transition to the region of positive adsorption (ATLC—Figs. 3*c* and 3*a*), where an increase of the molecular weight of the polymer entails a decrease of its R_f.

The free energies of the adsorption ($-\Delta F$) of the macromolecules can be readily evaluated from the thin-layer chromatograms. For this purpose, one may use the equation

$$R_f = \left(1 + \frac{V_p}{V_0} K_d\right)^{-1}, \tag{1}$$

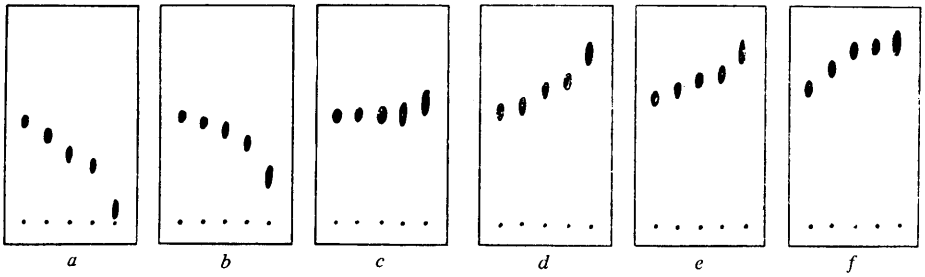

Figure 3. TLC of polystyrenes *5–9* (see Fig. 2) from left to right on KSK silica gel in the 40 : 16 : x cyclohexane + benzene + acetone system; x: *a*) 1.5; *b*) 1.8; *c*) 2.0; *d*) 2.2; *e*) 2.5; *f*) 2.8; with preliminary saturation of the plate in solvent vapour for 2 h.

where V_p/V_0 is the ratio of the volumes of the pore and interparticle spaces in the adsorbent, as well as the expression

$$K_d = \exp\left(-\frac{\Delta F}{kT}\right). \qquad (2)$$

Eqns.(1) and (2) make it possible to determine the ratio V_p/V_0, since we have $-\Delta F = 0$, $K_d = 1$, and

$$\frac{V_p}{V_0} = \left(\frac{1-R_f}{R_f}\right)_{-\varepsilon=-\varepsilon_{cr}} \qquad (3)$$

when $-\epsilon = -\epsilon_{cr}$.

Fig. 4[25] illustrates the experimental relation between $-\Delta F/kT$ and $-\epsilon$, calculated by Eqns. (1) and (2) for silica gels of different porosity. The observed relation is similar to the theoretical relation[23]. Fig. 4 shows clearly the presence of two energy regions corresponding to the adsorption of macromolecules with energies smaller and greater than $-\epsilon_{cr}$ (the regions of negative and positive adsorption). The experimental relations for PS with different molecular weights then make an intercept on the abscissa axis at the same point, corresponding to $-\epsilon_{cr}$. At this point the entropy losses ΔS by the macromolecule on adsorption are fully compensated by the increase of the enthalpy ΔH:

$$\Delta F(-\varepsilon) = \Delta F(-\varepsilon_{cr}) = \Delta H - T\Delta S = 0 \ .$$

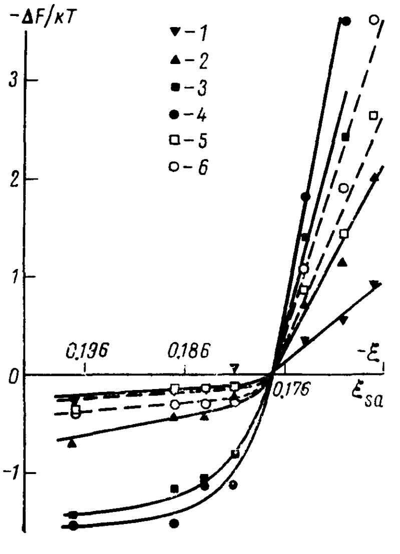

Figure 4. Dependence of the change in the free energy of PS macromolecules ($-\Delta F/kT$) on entering pores on the energies of the interaction of the macromolecular segment ($-\epsilon$) and solvent molecules (ϵ_{sa}) with the surface of the pores. Curves *1–4* represent data for KSK silica gel (pore diameter 100 Å) and curves *5* and *6* represent data for silochrome K-80 (pore diameter 500 Å); molecular weight of polystyrenes M_w: 1) 1.98×10^4; 2) 5.1×10^4; 3) and 5) 1.11×10^5; 4) and 6) 1.73×10^5.

It is possible to show with the aid of TLC on silica gels of different porosity using eluents of the same composition for the same values of $-\epsilon$) that, as the pore size increases, the TLGPC of polystyrene is transformed into ATLC at high acetone concentrations, i.e. with increase of pore size $-\epsilon_{cr}$ diminishes. The observation that, for high values of $-\epsilon$, the macromolecules enter small KSM silica gel pores and are adsorbed in the latter more strongly than in the large KSK and K-80 silica gel pores is of considerable interest[25]. This fundamentally new result conflicts with the results of a number of investigations[20] carried out in non-chromatographic concentration ranges, but is fully consistent with the theory[24].

Experiments[3] on the TLC of PS yielded a linear relation between $-\Delta F/kT$ and the number of segments (i.e. M_w) of the polymer (Fig. 5), which is consistent with the relation predicted by the theory[25]:

$$K_d = \exp(-\lambda_\varepsilon N), \qquad (4)$$

where λ_ϵ is the change in the free energy of the macromolecule per unit and N the number of polymer units. Using Eqn. (4), we can formulate an expression for R_f in the case of adsorption TLC of polymers:

$$R_f = \left(1 + \frac{V_p}{V_0}\exp(-\lambda_\varepsilon N)\right)^{-1}. \qquad (5)$$

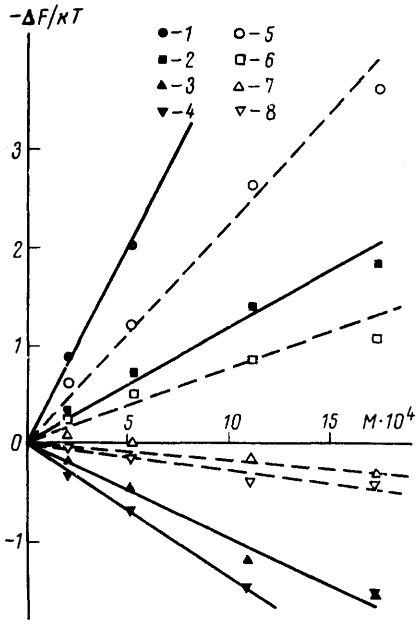

Figure 5. Dependence of the change in the free energy ($-\Delta F/kT$) of PS macromolecules on entering KSK silica gel (curves *1–4*) and silica gel K-80 (curves *5–8*) pores on the molecular weight. ϵ_{sa}: 1) and 5) 0.167; 2) and 6) 0.173; 3) and 7) 0.181; 4) and 8) 0.197.

Having differentiated Eqn. (5) with respect to N and λ_ϵ, we find that the sensitivity of R_f to the molecular weight of the polymer ($\partial R_f/\partial N$) decreases with increase of N and the dependence of $\partial R_f/\partial N$ on $-\lambda_\epsilon$ passes through an extremum near ϵ_{cr}. For each molecular weight there is a characteristic extremum in λ_ϵ, i.e. near the eluent composition;

consequently the region of the maximum sensitivity of TLC to the molecular weight of the polymer in each range of M_w values is characterised by the particular eluent composition, as can be seen in Fig. 2. The variation of the influence on R_f of the chemical composition of the polymer, characterised by λ_ϵ, i.e. of $\partial R_f/\partial\lambda_\epsilon$, also passes through a maximum. It follows from studies of ATLC that the sensitivity of R_f to the copolymer composition persists at least up to $M_w \simeq 5 \times 10^5$.

It has been suggested in the literature[18,28-30] that in ATLC polymers are fractionated on the basis of their chemical compositions and not their molecular weights. In reality, when a binary or ternary mixture of solvents, preferably containing an adsorption-active component, is used instead of a pure solvent, it is always possible to obtain the value of $-\epsilon$ necessary for the separation of polymers over a fairly broad range of molecular weights, with R_f in the range 0.1–0.8. The upper limit to the molecular weights in the separation of polymers by the ATLC method is set by the low rates of adsorption and desorption processes involving high-molecular-weight polymers. However, by introducing an adsorption-active component into the eluent, for example acetone, it is possible to increase this limit significantly (Fig. 2*c*).

III. THIN-LAYER CHROMATOGRAPHY BASED ON DIFFERENCES BETWEEN THE SOLUBILITIES OF POLYMERS

Inagaki and coworkers[14,28] proposed precipitation TLC as the main method for the separation of polymers on the basis of their molecular weights. Precipitation TLC has been used successfully by these and other investigations in the fractionation of homopolymers[14,28,31,32] and statistical copolymers[30] in terms of their molecular weights, for the separation of atactic and syndiotactic PMMA[15], for the fractionation of ST–MMA block copolymers[32], and for the separation of block copolymers of this type and PMMA.[33]

1. Characteristics of the Precipitation and Extraction TLC of Polymers

The elementary step in precipitation TLC involves the separation of the polymer solution into a dilute phase and a concentrated gel phase, which is precipitated on the surface of the adsorbent particles; the dilute phase is removed with the solvent stream and the chromatographic process is thus achieved. In order to carry out precipitation TLC (PTLC), it is necessary to suppress the adsorption of the polymer. Hence arise two requirements which must be met by eluents: they must be adsorption-active and must at the same time be poor solvents for the polymer (the latter may be assessed with the aid of the Flory–Huggins solubility parameter[34] χ, which is defined as the change in free energy, in units of kT, on transferring a solvent molecule from the pure solvent to the polymer solution). When $\chi > 0.5$, the solubility of the polymer falls and the formation of the gel phase begins.

According to the Flory-Huggins theory[34], the phase separation of the polymer solution (at a constant temperature) can occur under the influence of two factors: (1) with increase of χ, i.e. when $\chi > 0.5$ or (2) with increase of the polymer concentration in solution φ_p (for $\chi \simeq 0.5$). χ may be increased by raising the content of the precipitant in the eluent composition, while the bulk-phase concentration of the polymer may be increased by altering the phase ratio r (the ratio of the volume of the eluent to the weight of the adsorbent). Since the removal of the dilute polymer phase with the stream of eluent is accompanied by the formation of a gel phase in equilibrium with it only when χ and φ_p are varied, an essential condition for PTLC is the creation of a solvent concentration gradient (i.e. χ) and (or) the establishment of the given phase ratio r on the plate. Two procedures are used for this purpose: (1) by the reduction of the solubility of the polymer, as the eluent rises along the plate, owing to the evaporation of the solvent in the unsaturated chromatographic chamber and by its frontal separation on the adsorbent layer (intrinsic PTLC); (2) by applying to the chromatographic plate an eluent in which the content of the solvent is increased (the extraction version of PTLC).

Figure 6. TLC of PMMA on silica gel in the 29 : 71 chloroform + methanol system. Molecular weight of PMMA M_w: 1) 4.3×10^4; 2) 1.14×10^5; 3) 1.65×10^5; 4) 4.12×10^5.

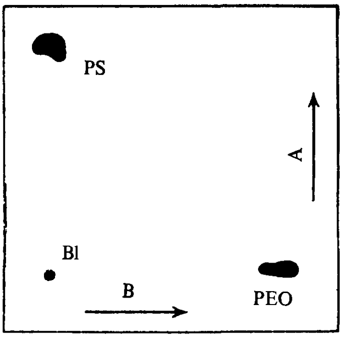

Figure 7. Two-dimensional TLC of a 50 : 50 ST-OE [EO?] block copolymer (Bl) on KSK silica gel in the 12 : 4 : 2 cyclohexane + benzene + acetone system in the *A* direction and in the 3 : 9 pyridine + water system in the *B* direction.

TLC based on the solubilities of polymers includes ETLC, where polymers with appreciably different solubilities are separated with the aid of a gradient-free eluent at the starting point on the "all or nothing" principle.

Examples of the extraction version of PTLC are provided by the separation of PS on the basis of their molecular weights following the addition to acetone of acetone–chloroform and acetone–toluene mixtures[31] and the separation of PMMA in the chloroform (solvent)–methanol (precipitant) system[14] (Fig. 6). An example of PTLC proper is the separation of PS in the 5 : 3 : 6 : 4 benzene–EMK–acetone–ethanol system, where the first two components are solvents and the last two are precipitants. Examples of ETLC are provided by the separation of isotactic and atactic PS and of the ST–EO block copolymer and the PS and PEO present in it[3] (Fig. 7). It has been stated in the literature that the effectiveness of fractionation on the basis of molecular weights is greater in ATLC and PTLC respectively in the regions where $M_w < 10^5$ and $M_w > 10^5$.[18,28-30] A combination of these methods is used in the study of the distribution in the polymer on the basis of its composition (ATLC) and its molecular weight (PTLC). For example, it has been used to separate statistical ST–BD copolymers in ethyl acetate and in the THF–methanol system[30]. The dependence of R_f on M_w and the mole fraction of ST is then determined by the equation $R_f = A + B[\mathrm{ST}] - C_2 \lg M_w$, where A, B, and C_2 are constants. Similarly PS with terminal COOH groups are separated on the basis of their functionalities following successive elution with benzene and chlorobenzene (ATLC) and on the basis of the molecular weights in the 1 : 10 THF–acetone system to which THF has been added (PTLC).[36] Other examples of the employment of precipitation TLC in the analysis of polymers are given in the Appendix (Table II).

It is noteworthy that the main application of the PTLC of polymers involves fractionation on the basis of the molecular weights and determination of the molecular weight distribution. The molecular weight distributions of polystyrene found with the aid of PTLC and by the GPC method in columns have been compared[16,37]. The results agreed satisfactorily, but there is no doubt that the TLC method is inferior to GPC as regards the speed and accuracy of analysis. In the fractionation of polymers on the basis of their molecular weights, it is desirable to employ two-dimensional PTLC with the simultaneous analysis of the inhomogeneity of the polymers with respect to composition by means of ATLC.

The decrease of the solubility of the polymer in the presence of the support[19], while the chemical nature of the adsorbent and its porosity have no effect on the separation of polymers with the aid of PTLC (i.e. the precipitation of the polymer takes place on the outer surface of the adsorbent grain[35]) is important for the understanding of the PTLC mechanism.

2. The Formation of False Chromatographic Bands in Precipitation TLC of Polymers

In TLC in a solvent–precipitate system where the solvent does not exhibit adsorption activity while the precipitant does possess it (for example, in the chloroform–methanol system for PMMA[14]) there are two methanol concentration ranges where its content is less than 5% (ATLC) and more than 70% (PTLC) and R_f for the polymer changes from 0 to 1 (Fig. 8). This finding explains the formation of double chromatographic spots on plates in the PTLC of polymers (Fig. 9).[33] A PMMA chromatogram has been obtained (Fig. 9) with the starting spots applied to the plate along the diagonal. Evidently, with increase of the distance of the starting zones from the line along which the plate is immersed in the solvent, the substance is, as it were, pumped from the starting spot to the upper spot, moving with the eluent surface. The essential feature of this phenomenon consists in the frontal separation of the eluent into the chloroform and chloroform–methanol zones. On reaching the starting point, the diffuse front of the second zone dissolves PMMA until the methanol concentration rises above 80%. Naturally, the lower the flow rate of the eluent, i.e. the higher the position of the polymer starting zone on the plate, the greater the proportion of the polymer which is able to dissolve and pass to the upper chromatographic spot and the lower the residual amount of the polymer at the starting point.

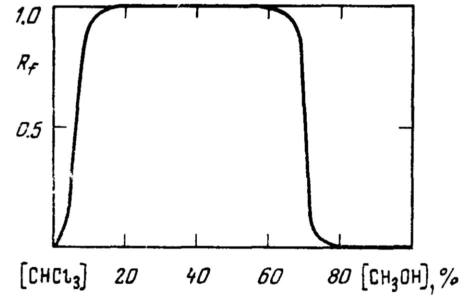

Figure 8. Dependence of R_f for PMMA with $M_w = 4.1 \times 10^5$ on the composition of the chloroform + methanol mixture in TLC on silica gel.

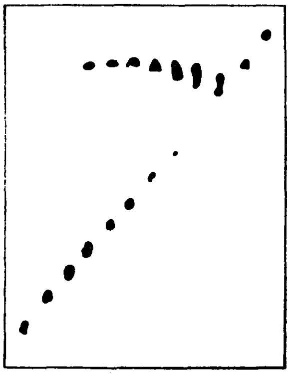

Figure 9. TLC for PMMA with $M_w = 10^5$ in the 6 : 16 chloroform + methanol system on KSK silica gel in an S-chamber (samples deposited along the diagonal of the plate).

IV. CONCENTRATION DEPENDENCE OF THE SHAPE OF THE CHROMATOGRAPHIC SPOT IN THE THIN-LAYER CHROMATOGRAPHY OF POLYMERS

The shape of the chromatographic spot is determined by the type of the adsorption isotherm (Fig. 10).[3] A concave isotherm is characteristic of weak adsorbability ($R_f \rightarrow 1$) and with increase of the concentration of the substance the chromatographic spot is extended towards the rear (Fig. 10*c*). A convex isotherm is characteristic of strong adsorbability ($R_f \rightarrow 0$) and with increase of concentration the chromatographic spot is extended forward (Fig. 10*a*). When $R_f \simeq 0.5$, the adsorption isotherm is close to linearity and the shape of the chromatographic spot depends little on the concentration of the substances (Fig. 10*b*). Two-dimensional spreading in TLC leads to additional concentration effects. Along the sides of the chromatographic zone, the concentration of the substance diminishes and hence the velocity of the zone is determined by a partition coefficient different from that in the central zone. As a result, the spot assumes a sharper shape: in the front and in the rear it is characteristic of convex and concave adsorption isotherms respectively. In precipitation TLC the higher the polymer concentration in the chromatographic spot, the lower the precipitant concentration corresponding to the polymer solubility threshold and the spot is more extended in the direction opposite to that of the motion of the polymer on the plate.

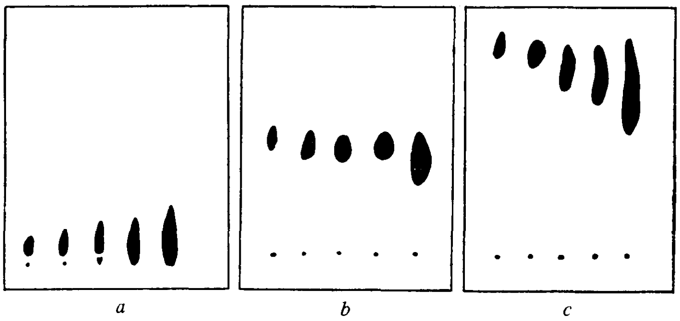

Figure 10. Concentration dependence of the shape of the chromatographic spot in TLC of PS with $M_w = 4 \times 10^5$ in cyclohexane + benzene + acetone systems: *a*) 12 : 4 : 0.25; *b*) 12 : 4 : 0.5; *c*) 12 : 4 : 1. 2, 5, 10, 20 and 40 μg of PS deposited from left to right.

The shape of the chromatographic spot in the TLC of polymers depends also on the characteristics of the viscous flow of the polymer solution along the plate. In the centre of the spot, where the polymer concentration is high, the velocity of the solvent is a minimum. In the peripheral regions it increases and reaches a maximum in the gaps between the chromatographic spots. As a result, the spot assumes a drop-like shape (Fig. 11)[4] characteristic of the streams formed when a viscous liquid flows past obstacles[38]. Under these conditions, the rear boundary of the spot undergoes additional sharpening by the incoming flow of liquid, which prevents the diffusional spreading of the spot, while in the front section of the zone the velocity of the diffusing molecules and the flow rate of the stream are added together[39]. These processes lead to instability of the chromatographic zone. It can assume an irregular shape and can actually be split into several spots moving separately.

V. TLC STUDY OF THE MICROSTRUCTURES OF POLYMERS

1. The Study of the Stereoregularity of Polymers

Inagaki and coworkers[15] showed that the separation of stereoregular polymers may be based on the differences between their solubilities. Using ethyl acetate as the eluent, Inagaki and coworkers succeeded in separating by ETLC [40] isotactic (*i*) PMMA, which remained in the starting spot, from syndiotactic (*s*) and atactic (*a*) PMMA, which moved with the solvent front. When the elution is carried out with acetone[41], *i*-PMMA is also desorbed, but the 1 : 1 stereocomplex of *i*-PMMA and *s*-PMMA remains at the starting point; thus 2 : 1 and 1 : 2 mixtures of these polymers appear on the chromatogram as two spots—at the starting point and near the solvent front. The lower spot represents the 1 : 1 stereocomplex and the upper spot corresponds to *i*-PMMA or *s*-PMMA respectively. Stereoblock PMMA with a high content of iso- and syndio-tactic triads can also be separated with the aid of TLC.[40]

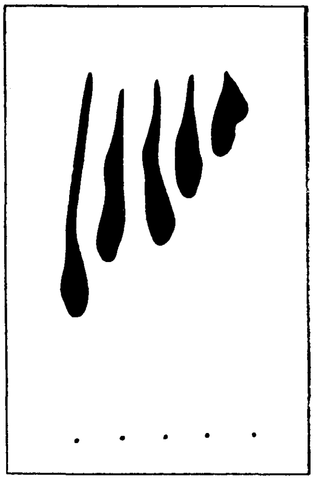

Figure 11. The "viscous" form of the chromatographic spot of PS with $M_w = 8.7 \times 10^5$ in TLC on KSK silica gel in benzene; 100, 40, 30, 20 and 10 μg of PS deposited from left to right.

We obtained analogous results[4] in the TLC of polystyrene (Fig. 9). It was shown that *a*-PMMA and *s*-PMMA may be separated[41] with the aid of ATLC in the ethyl acetate–isopropyl acetate system and with the aid of PTLC in the acetonitrile–methanol system. Under these conditions, R_f is found to depend not only on the content of syndiotactic triads (Ts) but also on M_w: $R'_f = 1.73\,[\mathrm{Ts}] - 0.51 \lg M_w - 2.2$ in the acetonitrile–methanol system and $R''_f = -1.74\,[\mathrm{Ts}] - 0.08 \lg M_w + 6.0$ in the ethyl acetate–isopropyl acetate system. [Ts] and M_w for PMMA may be determined to within approximately 10% with the aid of the above equations.

The conditions found for the isolation of *i*- and *s*-PMMA by ATLC were used for preparative isolation of *i*-PMMA from their mixture by adsorbing *i*-PMMA on silica gel from solution in chloroform. The *i*-PMMA obtained in this way was 80–90% pure[42].

2. The Study of the Regularity and Isomerism of Polybutadienes and Polyisoprenes

1,4-*trans*-, 1,4-*cis*-, and 1,2-Polybutadienes can be separated by ATLC in tetrachloroethane and by ETLC in pentyl chloride on silica gel and alumina plates[43]. This method may be used to test the homogeneity of the so-called equibinary PB in which 1,4-*cis*- and 1,2-vinylbutadiene units are present. In TLC in tetrachloroethane these polymers move with the solvent front; on the other hand, when the specimen is a mixture of 1,4-*cis*- and 1,2-PB, they are separated into the corresponding zones on the plate.

It has been shown[44] that 3,4-vinyl-PI can be separated from 1,4-*cis*- and 1,4-*trans*-PI with the aid of ATLC in tetrachloroethane, while in the 20 : 80 cyclohexane–*p*-xylene system 3,4-vinyl- and 1,4-*trans*-PI can be separated from 1,4-*cis*-PI.

3. TLC of Block Copolymers

The possibility of separating two-block and three-block ST–MMA copolymers with the aid of ATLC in gradient-free tetrachloroethane–EMK systems to which EMK is added has been demonstrated[32]. Under these conditions, R_f is independent of the molecular weight of the copolymer. Fig.12 shows[32] that R_f for ST–MMA copolymers having the same composition increases in the sequence statistical < three-block < two-block copolymers. ST–BD block copolymers can be separated by ATLC in the 9 : 1 cyclohexane–chloroform system with gradual addition of chloroform[11]. R_f for ST–BD copolymers increases in the following sequence: two-block (ST–BD) < three-block (ST–BD–ST) copolymers (i.e. two- and three-block ST–BD copolymers move on the plate in a sequence different to that of the analogous ST–MMA copolymers). In this chromatographic system R_f for the ST–BD copolymers is independent of their molecular weight. When PTLC is used in the 3 : 2 chloroform–methanol system with addition of methanol, the ST–BD block copolymers can be separated on the basis of their molecular weights.

The application of these chromatographic systems made it possible to establish with the aid of two-dimensional TLC that the Kraton 1101 industrial block copolymer consists of three components: two three-block copolymers having the same composition but different molecular weights and PS with $M_w = 10^4$. These data agreed with the results of GPC analysis using two detectors (refractometric and spectrophotometric), which permitted a direct determination of the compositions of the copolymers chromatographed.

The conditions found for the ATLC of ST–MMA copolymers, where R_f depends only on the copolymer composition, enabled Inagaki and coworkers[45] to suggest a method for the determination of the inhomogeneity of these copolymers with respect to composition (Section VII, 3), based on the densitometry of thin-layer chromatograms at two wavelengths: $\lambda_1 = 225$ nm (where the ST and MMA units absorb) and $\lambda_2 = 265$ nm, where only the ST units absorb. The distribution of two- and three-block ST–MMA copolymers with respect to composition, investigated by this method, showed that it corresponds fully to the distribution obtained by cross-fractionation and calculated on the assumption of a random mechanism of the coupling of the blocks in anionic polymerisation.

In the TLC of block copolymers one can use the precipitation mechanism instead of the adsorption mechanism. In a solvent which is ineffective in relation to one of the blocks the block copolymer enriched in this particular block then frequently undergoes selective precipitation. Thus, in order to separate PMMA from the ST–MMA block copolymer, a chloroform–methanol gradient system may be employed. Since PS is initially precipitated in this system and then PMMA, as the chloroform content is reduced, in the PTLC of PMMA and the ST–MMA block copolymer in an S-chamber, one can employ a system having a composition (with 72–80% of methanol depending on the molecular weight of PMMA) such that the copolymer remains at the start. $R_f < 1$ for PMMA under these conditions, since the concentration of methanol in the eluent becomes sufficient for the precipitation of PMMA at a certain height as a result of the gradual evaporation from the plate.

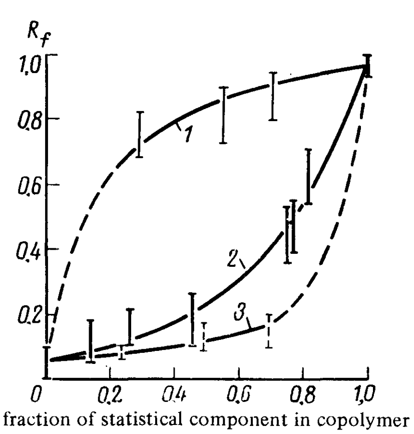

Figure 12. Separation of statistical (curve *1*), three-block (MMA–ST–MMA) (curve *2*), and two-block (curve *3*) ST–MMA copolymers using EMK gradients ranging from 0 to 2.5 in the EMK + carbon tetrachloride system.

In the study of block copolymers the determination of the admixture of homopolymers plays an important role. In this type of analysis of the EO–ST block copolymer use was made of two-dimensional ETLC [3] (Fig.7), which makes it possible to separate the corresponding homopolymers from the EO–ST block copolymer. This copolymer may be subjected to analogous analysis by one-dimensional TLC on microcrystalline cellulose in the 9 : 1 ethyl acetate–methanol system[46]. Under these conditions, PS moves with the solvent front, the block copolymer passes to the centre of the plate, and PEO remains at the start. Wesslen and Nansson[46] developed a preparative method for the isolation of the block copolymer by column chromatography: PS was separated by elution with ethyl acetate, the block copolymer was then eluted with a 4 : 1 mixture of ethyl acetate and methanol, and finally PEO was eluted with methanol; the column chromatography was checked by TLC.

4. TLC of Graft Copolymers

In the analysis of graft copolymers TLC is used to determine their purity, to detect the presence of homopolymers corresponding to the main and side chains, and to separate the polymers forming their grafted side chains (after the cleavage of the main chain of the graft copolymer) and the homopolymers present in the graft copolymer (Section VIII, 3).

The use of TLC for the solution of the first problem was first demonstrated[3] in the separation of the ST–MMA graft copolymer, PS, and PMMA. Methods have been proposed[47] for the separation of copolymers of PS grafted on CTA, PVA, PETP, and polyamide, and of PMMA grafted on PVA from the corresponding homopolymers with the aid of flow ATLC. The separation conditions discovered made it possible to proceed to preparative adsorption chromatography on columns, whereupon a PS–CTA graft copolymer contains less than 0.5–1% of impurities was obtained in quantitative yield.

It is of interest to use TLC in the study of impact-resistant PS. Here ETLC in EMK on silica gel[44] was employed to separate PS from the PS–PBD graft copolymer (see Appendix, Table III).

VI. THIN-LAYER CHROMATOGRAPHY OF OLIGOMERS

1. Principal Characteristics of the TLC of Oligomers

The TLC of many classes of oligomers has been described: polyols[48-58], polyethers[59-63], polyolefins[64], and polyamides[65]. Most of the studies demonstrated the possibility of separating oligomers differing in the number and structure of terminal groups. Many investigators[48-50, 58,61] demonstrated the independence of the chromatographic behaviour of oligomers of their molecular weights, while the differences in the R_f values are determined solely by the number of functional groups present in the oligomers. This makes it possible to achieve an extremely important form of the analysis of oligomers—the determination of their functionality[66], which is responsible for the quality of the high polymers obtained from oligomers, for example, polyurethane. On the other hand, substituted polyoxyethylenes can be separated on the basis of their molecular weights, with isolation of the individual polymer homologues in terms of the degree of polymerisation[12-15]. It has been shown[57] that the efficiency of the separation of polyols on the basis of their molecular weights is related to the type of substituent blocking the hydroxyl in the terminal units. The more hydrophobic the substituent (i.e. apparently the greater the bulk of the hydrocarbon group of the substituent and hence the lower the adsorbability of the terminal units), the greater the efficiency of the separation of the oligomers into individual homologues.

The characteristics of the adsorption of oligomers are associated with the presence of terminal functional groups. These terminal units as a rule show a greater adsorption activity than the central units of the oligomer and the change in the free energy of the latter on adsorption is determined mainly by the adsorption of the terminal groups. The free energy of adsorption ($-\Delta F$) of oligomers is associated with the decrease of the entropy ΔS, owing to the decrease of the number of possible conformations of the oligomer on adsorption, and with the increase of the enthalpy of the system $-\Delta H$ on formation of contacts between the units of one mole of the oligomer and the adsorbent surface:

$$-\frac{\Delta H}{RT}=N_A[(-\varepsilon_t)N_t+(-\varepsilon_c)(N-N_t)], \tag{6}$$

where $-\epsilon_t$ and $-\epsilon_c$ are the energies of the interaction of the terminal and central units with the adsorbent surface in units of kT, N and N_t are the total number of units and the number of terminal units in the oligomer molecule, and N_A is the Avogadro number. The partition coefficient in adsorption is expressed as follows:

$$K_d=\exp\left(-\frac{\Delta F}{RT}\right)=\exp\left(-\frac{N_A\Delta F_M}{RT}\right)=\exp\left(-\frac{\Delta F_M}{kT}\right), \tag{7}$$

where $-\Delta F_M$ is the free energy of adsorption of one molecule of the oligomer. One can specify an energy $-\epsilon_0$ such that the enthalpy of adsorption fully compensates the decrease of entropy and $-\Delta F_M = 0$. Then $-\Delta F/kT$ for the oligomer undergoing adsorption is

$$-\frac{\Delta F}{kT}=[(-\varepsilon_t)-(-\varepsilon_0)]N_t+[(-\varepsilon_c)-(\varepsilon_0)](N-N_t). \tag{8}$$

We shall consider the influence of the relative values of $-\epsilon_c$ and $-\epsilon_0$ (in TLC, we always have $-\epsilon_c > -\epsilon_0$) on the R_f of oligomers in ATLC: $R_f = 1/[1 + (V_p/V_0)\exp(-\Delta F_M/kT)]$. There can be three instances of the dependence of R_f on N (i.e. on the molecular weight of the oligomer):

(1) $(-\epsilon_c) > (-\epsilon_0)$; $-\Delta F/kT = [(-\epsilon_t) - (-\epsilon_0)]N_t + [(-\epsilon_c) - (-\epsilon_0)](N - N_t)$, where R_f decreases with increase of N;

(2) $(-\epsilon_c) < (-\epsilon_0)$; $-\Delta F/kT = [(-\epsilon_t) - (-\epsilon_0)]N_t - [(-\epsilon_c) - (-\epsilon_0)](N - N_t)$, where R_f increases with increase N;

(3) $(-\epsilon_c) = (-\epsilon_0)$; $-\Delta F/kT = [(-\epsilon_t) - (-\epsilon_0)]N_t$, where R_f is independent of N and is determined by the number of terminal groups N_t.

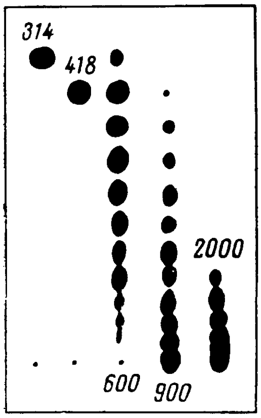

Figure 13. TLC of oligomers: PS with M_n = 314, 418, 600, 900, and 2000 in the 14:3 cyclohexane + benzene system on KSK silica gel.

It is noteworthy that in the absence of functional groups ($N_t = 0$) only the dependence of the first type can be observed. Fig. 13 illustrates chromatograms of PS oligomers of this type[67,68]. Clearly the dependence of R_f on the molecular weight of oligomers with $N_t = 0$ will be manifested to the greatest extent. On the other hand, when the oligomer contains functional groups, the dependence of R_f on the molecular weight becomes less marked with increase of the differences between $-\epsilon_t$ and $-\epsilon_c$.

Fig. 14 illustrates the TLC of poly(ethylene oxide) with M_n = 300, 400, and 600 in chromatographic systems where the dependence of R_f on the molecular weight is of the first, second, and third type[67]. Attention should be drawn to the correspondence of the polymer homologues in poly-(ethylene oxides) with different molecular weights. The dependence of R_f on the molecular weight of poly(ethylene oxide) shown in Fig. 14*b* is characteristic of the molecular sieve effect, but the mechanism of TLC is in this case different since the oligomers investigated begin to be excluded from the pore space of these adsorbents when the molecular weight exceeds 10^4. The moon shape of the chromatographic spot is associated (see above) with the convex adsorption isotherms for polyols. It is noteworthy that an effective separation on the basis of molecular weights of oligomers with weakly adsorption-active central units (for example, polydimethylsiloxanediols) is impossible without blocking the terminal groups. However, even when the terminal hydroxyls are blocked, (for example, by the dinitrobenzoic acid residue) only the second type of dependence of R_f on the molecular weight can be obtained.

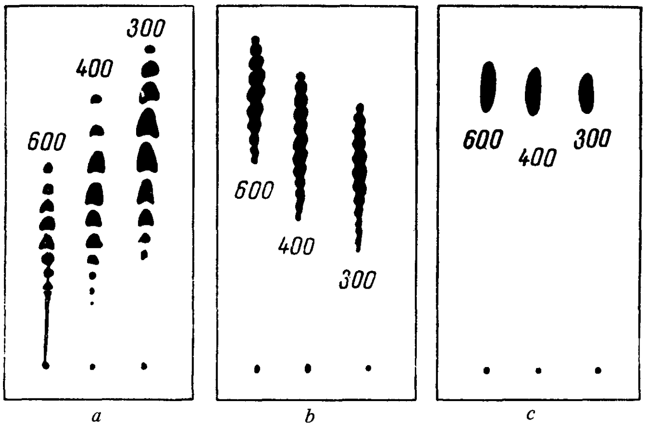

Figure 14. TLC of poly(ethylene oxides) with M_n = 300, 400, and 600: *a*) on KSK silica gel in the 0.1 : 10 pyridine + water system; *b*) on alumina in the 10 : 1 chloroform + ethanol system; *c*) on KSK silica gel in the 5 : 1 chloroform + pyridine system.

2. Separation of Oligomers on the Basis of Their Functionality

The separation of oligomers on the basis of their functionality in the absence of a dependence of R_f on the molecular weight (third type of dependence of R_f for the oligomer on the molecular weight) is of great practical interest. The possibility of separating mono-ols, diols, and triols over a wide range of molecular weights is illustrated in Fig. 15 in relation to polyoxypropylenepolyols (POPP).[68] This method for the determination of the functionality of oligomers makes it possible to separate linear and branched oligomers differing in the number of terminal functional groups. The separation of linear and branched oligomers with the same molecular weight is of great analytical interest, because it has been established[69] that in GPC they emerge with the same retention volumes. Thus the molecular weight distribution of oligoethers obtained with the aid of GPC may be significantly supplemented by information about the distribution of branched polyfunctional oligoethers in the specimen analysed.

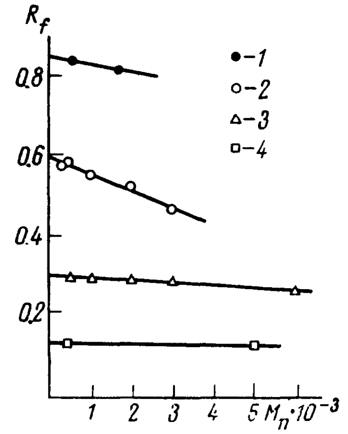

Figure 15. Dependence of R_f for polyoxypropylenepolyols (POPP) on their molecular weight and functionality on KSK silica gel in ethyl acetate saturated with water and containing 2% EMK: 1) mono-ols; 2) diols; 3) triols; 4) pentols.

VII. DETERMINATION OF POLYMER MOLECULAR WEIGHT AND COMPOSITION DISTRIBUTIONS FROM THIN-LAYER CHROMATOGRAPHIC DATA

1. Quantitative Interpretation of Thin-Layer Chromatograms of Polymers

Two fundamentally different methods for the quantitative analysis of thin-layer chromatograms are known[70]. The first is based on the extraction of the substance from the layer of adsorbent on the chromatographic plate with its subsequent determination, and the second involves the analysis of the substance directly in the chromatographic spot *in situ* from the distribution of the concentrations of the compounds in the spot[71,72] or from its size[73,74], the second method being more accurate and sensitive. For quantitative calculations on chromatograms of polymers from the distribution of concentrations or from the size of the spot, it is necessary to be able to view the chromatogram in visible light (i.e. it must be made visible), photographed, and then scanned to determine the distribution of the polymer concentrations in the chromatographic spot, or or to obtain with the aid of high-contrast photography the image of the polymer zone with distinct boundaries and, having measured the distance between the latter, to find the distribution of the spots with respect to size. Having at one's disposal more sophisticated methods and equipment, for example, luminescence and ultraviolet photographic techniques and scanning ultraviolet densitometers and fluorimeters, it is possible to reduce the number of stages required for quantitative analysis. Each stage introduces its own error into the result, but in certain cases the more complex procedure has advantages over the simpler method. For example, the linear relation between the blackening occurring when the spot is made visible by means of a corroding reagent and the polymer concentration in the spot is retained up to a concentration of 200 μg cm^{-2} in photodensitometry in the visible part of the spectrum, which is much higher than in the direct densitometry in the ultraviolet[2,3,7,16,40]. Furthermore, direct densitometry is possible only when the polymer contains chromophores strongly absorbing ultraviolet light, for example, styrene units. In this case the linear dependence of the signal on the amount of substance is maintained up to 100 μg cm^{-2}. Direct densitometry (particularly in reflected light) suffers also from other disadvantages, associated with the mutual influence of the monomer units of the polymer on their extinction and the preferential accumulation of the polymer in the lower layer of adsorbent adjoining the glass support. On the other hand, direct densitometry in the ultraviolet made it possible to suggest an absolute method for the determination of the inhomogeneity of copolymers with respect to composition by scanning their chromatographic zones on the plate at two wavelengths.

An interesting and promising version of quantitative TLC of polymers when the latter are separated into discrete zones involves the use for this purpose of a flame-ionisation detector (FID), the quartz plate with the deposited layer of silica gel being drawn directly through the flame[72].

In the analysis of radioactive polymers by TLC the method of lumoautoradiography[73], which makes it possible to determine up to 10^{-9} c of tritium without using complex apparatus, may prove to be very useful.

It is possible to distinguish the following varieties of quantitative TLC: (a) in terms of the method used to detect the chromatographic spots (by making them visible, by direct photography, and by direct detection on scanning); (b) in terms of the photographic process (photography in the visible or ultraviolet regions, lumoautoradiography, luminescence photography, equidense photography and ultrahigh-contrast photocopying); (c) in terms of the type of scanning (direct scanning of the chromatogram or of its photographic image); (d) in terms of the type of detecting system (detection using photometry, fluorimetry, radiometry, or a flame-ionisation detector); (e) in terms of the method used to carry out calculations on the chromatograms (based on the distribution of the concentrations of the given substance and the dimensions of the spot).

Evidently different combinations of these processes make it possible to obtain a multiplicity of different versions of quantitative TLC, about which the following comments may be made: methods based on procedures for rendering the chromatograph visible and direct photography consist of many stages and are therefore very time consuming. However, these methods, particularly those involving calculations on chromatograms based on the size of the spot, do not require expensive equipment. On the other hand, such equipment (scanning ultraviolet densitometers, fluorimeters, radiometers, FID) makes it possible to employ high-speed methods for the direct scanning of thin-layer chromatograms with an improved accuracy of the analysis. Methods involving ultraviolet and luminescence photography of chromatograms and lumoautoradiography occupy an intermediate place (as regards the speed of analysis and the complexity of equipment). Less expensive photometers, scanning in the visible region of the spectrum, are used in this case.

Methods for calculations on chromatograms, based on scanning and the determination of the size of the chromatographic zone, are considered below in relation to the analysis of the polydispersity of polymers.

As can be seen from the foregoing considerations, in order to determine the distribution of the molecular weights or compositions from TLC data, it is necessary (a) to make the polymer zone visible on the chromatogram (by dyeing it)§, (b) to determine the dependence of R_f for the polymer on the fractionating **X** (the molecular weight of the polymer) or on the composition of the copolymer, i.e. $R_\mathrm{f}(X)$ must be found, (c) to measure the dependence of the sensitivity of the detection (the ratio of the surface concentration of the given substance c to the colour intensity i) on R_f, i.e. to determine $(\mathrm{d}c/R_\mathrm{f})\mathrm{d}i$, (d) to measure the distribution of the colour intensity in the section of the chromatographic spot along the y axis, in the direction of motion of the spot, as a function of R_f, i.e. $I = I(R_\mathrm{f})$, where $I(R_\mathrm{f}) = \int\limits_{-\infty}^{+\infty} i(R_\mathrm{f}, y)\mathrm{d}y$, (e) to determine the distribution of the polymer in the chromatographic spot along the x axis, i.e. $Q(R_\mathrm{f}) = I(R_\mathrm{f})\colon (\mathrm{d}c/R_\mathrm{f})\mathrm{d}i$, where $\mathbf{Q}\int\limits_{-\infty}^{+\infty} c(y)\mathrm{d}y$, and finally (f), knowing $R_\mathrm{f}(x)$, to obtain the normalised differential distribution of the molecular weights of the polymer or the compositions of the copolymer:

$$P(X) = \tilde{Q}(R_f)\cdot\left|\frac{\mathrm{d}R_f}{\mathrm{d}X}\right|, \tag{10}$$

where $\tilde{\mathbf{Q}}(R_\mathrm{f})$ is the normalised distribution $Q(R_\mathrm{f})$:

$$\tilde{Q}(R_f) = Q(R_f)\Big/\int\limits_0^1 Q(R_f)\,\mathrm{d}R_f,$$

$$\int\limits_0^1 \tilde{Q}(R_f)\,\mathrm{d}R_f = 1.$$

In the study of narrowly disperse polymers it is necessary, in addition, to correct $Q(R_\mathrm{f})$ for chromatographic spreading—for example by means of two-dimensional chromatography (Fig. 16). The chromatogram of the polymer along the first direction, which is homogeneous with respect to the molecular weight (composition) along the spot diameter, may be regarded as the starting zone for chromatography in the second direction.

The difference between the dispersions of the zones at the finish and at the start in the direction of the second chromatographic process constitutes the dispersion of the chromatographic spreading. The correction may be applied in the simplest way by substracting the dispersion

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§A 1% solution of iodine in methanol[2], a saturated solution of Thymol Blue in 50% aqueous ethanol with subsequent treatment with 3 N H_2SO_4,[37] a 5% solution of $KMnO_4$ in concentrated H_2SO_4,[3] and, for oxygen-containing polymers, Dragendorff reagents[3] and iodine vapour[46] are most frequently used for this purpose. It is possible to detect PS on plates from the extinction of the luminescence due to a phosphor introduced into the chromatographic layer and excited with ultraviolet radiation at 254 μm.

of the chromatographic spreading from the dispersion of the distribution, or by a more complex and rigorous procedure, as in the analysis of the molecular weight distribution of polymers by the GPC method[75].

The normalised integral distribution $P(X) = \int_0^x F(X')\,\mathrm{d}X'$ and the weight-average quantity $\bar{X} = \int_0^\infty XF(X)\,\mathrm{d}X$ may be obtained from the weight distribution of the polymer $P(X)$ [Eqn. (10)].

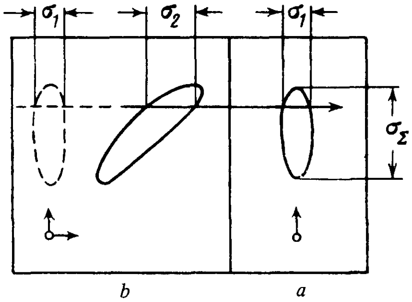

Figure 16. Determination of the chromatographic spreading in TLC: *a*) chromatogram along the first direction; *b*) two-dimensional chromatogram.

2. Photometric Method for Quantitative TLC of Polymers

In the photometric scanning of the polymer zone along the chromatographic axis (x), multistep scanning with an accurate light probe and integration of the signal with respect to the y axis, perpendicular to the chromatographic axis, is necessary in order to obtain accurate results. These integral properties represent the distribution $I(R_f)$ with an accuracy which is inversely proportional to the size of the step Δx. In order to determine the distribution of the compositions of the copolymers (provided that R_f for the copolymer is independent of its molecular weight), the method based on the scanning of the chromatographic plate at two wavelengths (265 and 225 nm), at which the molar extinction coefficients of the copolymer components differ markedly, has been proposed[45]. The absorption I at point x, corresponding to the fraction X of ST in the copolymer is then given by $I'(x) = X\epsilon'_{\mathrm{ST}}W(x)$ for $\lambda' = 265$ nm and $I''(x) = [X\epsilon''_{\mathrm{ST}} + (1 + X)\epsilon''_{\mathrm{MMA}}]W(x)$ for $\lambda'' = 225$ nm, where $W(x)$ is the amount of polymer in the region $(x \pm \Delta x)/2$ and ϵ is the molar extinction coefficient.

Having determined the areas A' and A'' under the densitograms of the polymer, using $I'(x)$ and $I''(x)$, and knowing $(\epsilon''_{\mathrm{ST}}/\epsilon''_{\mathrm{MMA}})$ and $(\epsilon'_{\mathrm{ST}}/\epsilon''_{\mathrm{MMA}})$, it is then possible to calculate the following characteristics of the copolymer:

(a) the normalised weight distribution of the copolymer $\tilde{P}(X)$:

$$\tilde{P}(X) = \frac{W(x)}{\sum\limits_i W_i(x)} = \frac{[1-(\varepsilon''_{\mathrm{ST}}/\varepsilon''_{\mathrm{MMA}})]\,I'(x) + (\varepsilon'_{\mathrm{ST}}/\varepsilon''_{\mathrm{MMA}})\,I''(x)}{[1-(\varepsilon''_{\mathrm{ST}}/\varepsilon''_{\mathrm{MMA}})]\,A' + (\varepsilon'_{\mathrm{ST}}/\varepsilon''_{\mathrm{MMA}})\,A''}; \tag{11}$$

(b) the calibration relation $X(x)$:

$$X(x) = \frac{I'(x)}{[1-(\varepsilon''_{\mathrm{ST}}/\varepsilon''_{\mathrm{MMA}})]\,I'(x) + (\varepsilon'_{\mathrm{ST}}/\varepsilon''_{\mathrm{MMA}})\,I''(x)}; \tag{12}$$

(c) the average composition of the copolymer $\bar{X}$:

$$\bar{X} = \frac{A'}{[1-(\varepsilon''_{\mathrm{ST}}/\varepsilon''_{\mathrm{MMA}})]\,A' + (\varepsilon'_{\mathrm{ST}}/\varepsilon''_{\mathrm{MMA}})\,A''} \tag{13}$$

without using reference copolymer specimens for the calibration of $X(x)$. The parameters $\epsilon'_{\mathrm{ST}}/\epsilon''_{\mathrm{MMA}}$ may be determined by Eqn. (12) from the known values of $\epsilon''_{\mathrm{ST}}/\epsilon''_{\mathrm{MMA}}$ and the average composition of the copolymer $\bar{X}$ determined independently.

3. Analysis of the Distribution of a Polydisperse Polymer Along the Width of the Chromatographic Zone

Since the distribution of the substance along the y axis in TLC is always described by a Gaussian curve, it is possible to determine the amount of substance in the given section (ith along the x axis) of the polymer zone on the chromatographic plate, having measured the width of the zone at a specific boundary (limiting detectable) concentration C_{b}. For a Gaussian distribution of the substance, we have

$$C_{\mathrm{b}} = C_{m,i}\exp\left(-\frac{y_i^2}{8\sigma_{y,i}^2}\right), \tag{14}$$

where $C_{\mathrm{m,i}}$ and $\sigma^2_{\mathrm{y,i}}$ are the concentration of the polymer at the maximum and the variance of the distribution in the ith (along the x axis) section of the zone and y_{i} is the distance along the y axis between the points C_{b} (the width of the zone in the ith section). The amount of substance in the ith section with the width Δx is then expressed as follows:

$$W_i = \sqrt{2\pi}\,\bar{C}_{m,i}\bar{\sigma}_{y,i}\,\Delta x = \sqrt{2\pi}k_iD_{\mathrm{b}}\,\sigma_{yi}\,\Delta x\exp\left\{\frac{\bar{y}_i^2}{8\bar{\sigma}_{y,i}^2}\right\}; \tag{15}$$

where the width of the zone $\bar{y}_{\mathrm{i}}$ and the variance $\bar{\sigma}^2_{\mathrm{y,i}}$ are averaged with respect to Δx and C_{b} is replaced by the corresponding optical density D_{b} ($C_{\mathrm{b}} = k_{\mathrm{i}}D_{\mathrm{b}}$, where k is a coefficient, which is constant for a homopolymer and which depends on the composition for a copolymer). In order to be able to use Eqn. (15), it is necessary to determine $\bar{\sigma}_{\mathrm{y,i}}$ having expressed it in terms of the experimental width of the chromatographic zone $\bar{y}_{\mathrm{i}}$. For this purpose, one can employ two procedures: (a) two chromatograms of the polymer containing different amounts of the substance, Q_1 and Q_2, are obtained, whereupon in each ith section in the two chromatographic zones the ratio of the amounts of the substance $W'_{\mathrm{i}}/W''_{\mathrm{i}} = Q_1/Q_2$, or (b) the polymer chromatogram is photographed with two different exposures, so that the contour of the spot corresponds to different values of C_{b} (i.e. D_{b}) and the ratio $D'_{\mathrm{b}}/D''_{\mathrm{b}}$ is determined.

The corresponding formulae for the calculation of the distribution $\tilde{P}_{\mathrm{i}} = W_{\mathrm{i}}/\sum\limits_{\mathrm{i}} W_{\mathrm{i}}$ by methods (a) and (b) are as follows:

$$\text{(a)}\ \tilde{P}_i = \frac{[ka^{1/2}b^{y_1^2/a}]_i}{\sum\limits_i [ka^{1/2}b^{y_1^2/a}]_i\Big|_{b=e}} = \frac{[ka^{1/2}\exp(y_1^2/a)]_i}{\sum\limits_i [ka^{1/2}\exp(y_1^2/a)]_i}, \tag{16}$$

$$a = y_1^2 - y_2^2,\quad b = Q_1/Q_2;$$

$$\text{(b)}\ \tilde{P}_i = \frac{[k(a')^{1/2}c^{(y')^2/a'}]_i}{\sum\limits_i [k(a')^{1/2}c^{(y')^2/a'}]_i},$$

$$a' = (y')^2 - (y'')^2,\quad c = D'_{\mathrm{b}}/D''_{\mathrm{b}}. \tag{17}$$

If method (a) is used to determine $\tilde{P}_i$, it is convenient to employ chromatograms on which polymers have been deposited in proportions $Q_1/Q_2 = e$, whereupon Eqn. (16) for $\tilde{P}_i$ simplifies.

As already stated, k = const. in the TLC of homopolymers or copolymers with narrowly disperse compositions and may be omitted from Eqns. (16) and (17). In the analysis of copolymers with polydisperse compositions, it is necessary to take into account the dependence of k on the composition of the copolymer (or R_f) and P_i must be calculated from Eqns. (16) and (17).

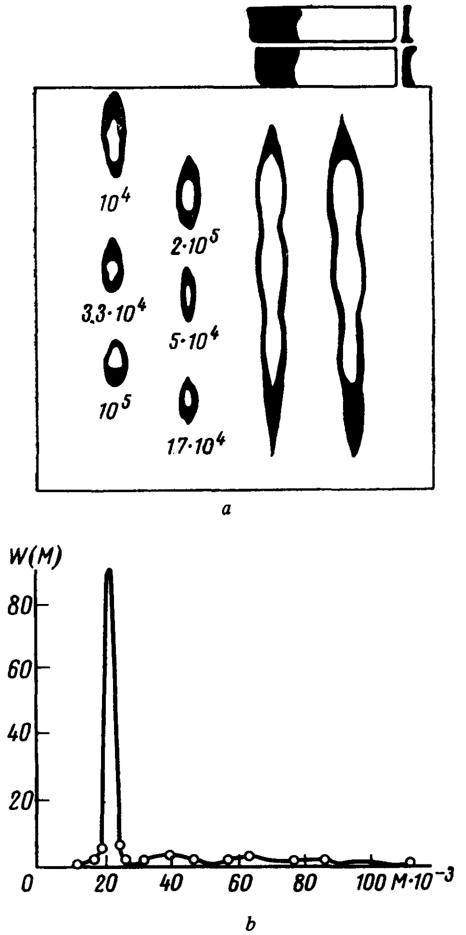

Figure 17. Determination of the molecular weight distribution in polystyrene by the equidense method: *a*) equidense representation of the chromatograms of PS specimens at two concentrations in the 12 : 4 : 0.9 cyclohexane + benzene + acetone system (on the left—chromatograms of reference PS specimens; above—image of optical wedge); *b*) molecular weight distribution in polystyrene.

Among the equations presented for the calculation of P_i, Eqn. (17) is of great interest, since its application requires only one chromatogram and there are no errors associated with the inaccuracy in the deposition onto the plate of calculated amounts of the polymers, Q_1 and Q_2, and with concentration effects distorting the shape of the chromatographic spot. In order to employ Eqn. (17), it is necessary to know D_b. An equidense method of obtaining the images of the chromatographic spot, based on the Sabatier phenomenon, which is well known in photography[76] (consisting in the complete or partial reversal of a briefly developed image under the influence of secondary illumination), was devised for this purpose[4]. An equidense image is achieved if a print is obtained, with a certain exposure, from the object for which photometric measurements are being made (the negative, in our case the thin-layer chromatographic plate), on a high-contrast photographic material, is developed for a short time, and, without fixation, is re-exposed to uniform secondary illumination. After redevelopment, the images of the chromatographic spots (equidense images) consist of pale contours of the spots against a dark background. The optical density D of the given equidense image of the object is determined by the duration of the first exposure. By varying this duration, it is possible to obtain equidense images corresponding to different optical densities $D_b^{(i)}$, which can be readily determined by photographing a calibrated optical wedge together with the object for which photometric measurements are made. In order to increase the contrast of the image, it is useful to photocopy the equidense image on an ultrahigh-contrast photographic material, which yields black equidense images against a light background.

The accuracy of the equidensitometric method of quantitative analysis discussed above was tested[4] by determining on the chromatograms the ratios of two polymers whose mixture had been deposited on the plate in proportions Q'/Q''. The ratios of 2.48 and 0.592 obtained agree satisfactorily with the ratios Q'/Q'' of the polymers in the samples (2.5 and 0.6). Fig. 17 illustrates an example of the analysis of the molecular weight distribution of PS by the equidensitometric method[4]. It is noteworthy that, owing to the relatively low sensitivity of the width of the chromatographic spot to the amount of substance it contains, the method described is inferior as regards accuracy to densitometric scanning methods in quantitative analysis. On the other hand, by virtue of the enhanced dependence of y on q on the wings of the curve, which is characteristic of a Gaussian distribution, the proposed method is particularly sensitive to the determination of microimpurities.

4. Determination of the Distribution of the Molecular Weights of Oligomers Using Equidense Images of Thin-Layer Chromatograms

A characteristic feature of the TLC of oligomers is the discrete nature of the chromatographic zones of individual polymer homologues up to $N \leqslant N'$, where $N' = 10-12$. Polymer homologues with higher molecular weights ($N > N'$) are chromatographed in the form of a continuous zone, which may be analysed in the same way as the chromatograms of high-molecular-weight polymers. If the limiting detectable concentration of the substance on the chromatograms is denoted by C_b, then the equation of the ellipse surrounding the chromatographic spot (x_b, y_b) is[77]:

$$C_b = \frac{q}{2\pi\sigma_x\sigma_y}\exp\left[-\frac{1}{2}\left(\frac{x_b^2}{\sigma_x^2}+\frac{y_b^2}{\sigma_y^2}\right)\right], \qquad (18)$$

where q is the amount of substance in the chromatographic spot and σ_x^2 and σ_y^2 are the variances of the distribution of the substance along the x and y axes. By denoting the half-axes of the ellipse by x_0 and y_0 (for $y = 0$ and $x = 0$ respectively), we obtain from Eqn. (18)

$$\frac{x_0^2}{\sigma_x^2} = \frac{y_0^2}{\sigma_y^2}. \qquad (19)$$

Using Eqn. (18) with $x_b = x_0$ and $y = 0$, and replacing σ_y with the aid of Eqn. (19), we have

$$q = 2\pi C_b \sigma_x^2 \frac{y_0}{x_0} \exp\left[\frac{1}{2}\frac{x_0^2}{\sigma_x^2}\right] = 2\pi k D_b \sigma_x^2 \frac{y_0}{x_0} \exp\left[\frac{1}{2}\frac{x_0^2}{\sigma_x^2}\right]. \qquad (20)$$

If two equidense images of the chromatogram with optical densities D'_b and D''_b are used, it is possible to obtain with the aid of two corresponding equations of type (20) an expression for q which includes only the experimentally determined quantities D_b, x_0, and y_0, obtained for two exposures:

$$q = 2\pi k D'_b \frac{(x''_0)^2 - (x'_0)^2}{2\ln\left[\frac{D'_b}{D''_b}\cdot\frac{y'_0/x'_0}{y''_0/x''_0}\right]} \cdot \frac{y''_0}{x''_0}\left(\frac{D'_b}{D''_b}\cdot\frac{y'_0/x'_0}{y''_0/x''_0}\right)^{\frac{x'_0}{(x''_0)^2-(x'_0)^2}}. \qquad (21)$$

It is also possible to find the amount of substance in the unresolved spots on the chromatograms (where $i > N'$). Using the $R_f(i)$ calibration relation in the form of a second-degree polynomial $R_f(i) = a + bi + ci^2$, where the coefficients a, b, and c are obtained by the method of least squares, we find the values of R_f for $i > N'$. Next, linear extrapolation (valid for $R_f < 1/3$) yields the values of x'_i, x''_i, y'_i, and y''_i for $i > N'$, using the values of the above quantities for $i = N'$ and $i = N' - 1$.

5. Quantitative Determination of Low-Functional Impurities in Polyoxypropylenepolyols with the Aid of TLC

A method based on the dependence of the mobility of the chromatographic spot on its oligomer content is used for the quantitative determination of low-functional components in polyoxypropylenepolyols[69]. The chromatographic spots of polyoxypropylenepolyols have a sharpened forward "tip" with a sharply defined leading boundary, while the rear front is diffuse. As stated above, this shape of the chromatographic zone is due to the concentration effects associated with a convex adsorption isotherm. It is natural to employ the chromatographic mobility of the "tip" of the chromatographic spot, which is related to the polymer concentration; R_f for the tip may be measured accurately in order to determine the amount of oligomer which it contains (under conditions such that R_f is independent of the molecular weight). An experimental test showed that this type of relation does exist (Fig. 18).[69] It is linear and retains a constant slope in a concentration range corresponding to two orders of magnitude, the slope of the straight line being related to the molecular weight of polyoxypropylenepolyol and the distance traversed by the substance on the chromatographic plate. A similar relation may be obtained theoretically on the basis of a simplified model of the ATLC of oligomers, where the adsorption is characterised by the Freundlich equation.

The proposed method for the quantitative analysis of thin-layer chromatograms is distinguished by its extreme simplicitiy; its error does not exceed 2–3%. Admixtures ($\leq$ 1–2%) of the mono-ol and diol in the specimens of polyoxypropylenepolyols can be determined by the above procedure[69].

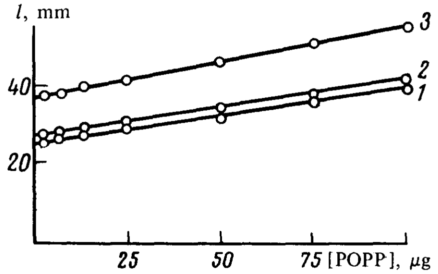

Figure 18. Dependence of the length of the chromatographic spot l on the amount of POPP with different M_n 1) 10^3; 2) 425; 3) 10^3 (40% EMK was added to the system) in TLC on silica gel in ethyl acetate saturated with water and containing 2% EMK.

6. The Use of a Scanning Flame-Ionisation Detector for the Quantitative TLC of Polymers with Separation of the Components into Individual Zones

The employment of a TLC–FID combination for the quantitative analysis of polymers, separated into individual zones, i.e. for the investigation of mixtures of fairly heterogeneous polymers has been described. The system described by Padley[72], where TLC is carried out on a quartz rod 0.45 mm in diameter coated by a layer of silica gel 75 μm thick, is used for this purpose; the polymer is deposited in an amount of several μg. After the completion of chromatographic process, the quartz rod is drawn through an FID during several tens of seconds.

The TLC–FID combination[44] has been used to determine the PS impurity in a copolymer obtained by grafting PS on to CTA, PS being separated by flow ETLC in EMK, and for the analysis of the functionality (the content of COOH and OH groups) of low-molecular-weight rubbers using the 100 : 1 carbon tetrachloride–THF system, in which PB molecules were separated into bifunctional molecules ($R_f = 0$), monofunctional molecules ($R_f = 0.3$), and molecules without functional groups ($R_f = 1.0$).

VIII. COMBINED CHROMATOGRAPHIC METHODS FOR THE ANALYSIS OF COMPLEX POLYMER SYSTEMS INVOLVING THIN-LAYER CHROMATOGRAPHY

In the synthesis of complex polymer systems, such as block copolymers, graft copolymers, and branched homopolymers the corresponding linear homopolymers are obtained together with the main product, which is characterised by its polydispersity with respect to molecular weight and composition (type of branching). The study of such polydisperse systems has constituted hitherto an extremely complex and laborious task and frequently could not be achieved at all by the classical methods for the analysis of polymers. Important results in this field may be obtained by using a combination of chromatographic methods for the analysis of polymers, GPC for the micropreparative fractionation of polymers involving the determination of the hydrodynamic radii R_s of the fractions obtained, TLC for the qualitative and quantitative analysis of the structural and chemical heterogeneity of the fractions, and pyrolytic gas chromatography (PGC) for the determination of their overall composition. The PGC method is unequalled under these conditions as regards the sensitivity of the analysis (it requires an amount of substance of the order of several μg) and as regards the accuracy of the determination of the composition of copolymers with a component ratio less than 1/20–1/50.[78]

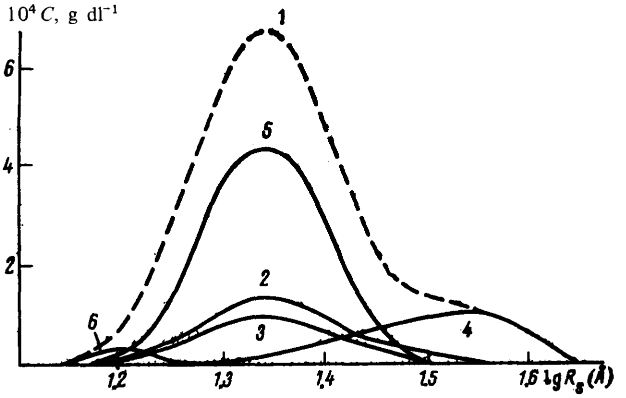

Figure 19. Concentration distribution curves for a PS specimen (curve *1*) and its components (curves *2–6*) as a function of the logarithm of the hydrodynamic radius lg R_S.

1. The Study of Mixtures of Linear and Branched Polymers by Gel-Permeation and Thin-Layer Chromatographic Methods

The possibility of studying a mixture of linear and branched PS using GPC and TLC has been demonstrated[79]. The micropreparative fractionation of the PS investigated has been achieved by means of GPC with determination of the hydrodynamic radius R_s of each fraction. For this purpose, use was made of the calibration relation obtained for linear PS specimens. Next, the GPC fractions were studied by ATLC methods in the 12 : 4 : γ cyclohexane–benzene–acetone system on KSK silica gel plates. In each fraction several components were detected with different dependences of R_f on the acetone content in the system (γ).[78] Some of these components behave similarly to the linear PS standards; they were identified as linear PS. Others show a weaker dependence of R_f on γ; these components were identified as branched PS and it was suggested that the differences between the adsorbabilities of linear and branched PS must increase with increase of the degree of branching. The GPC fractions were analysed quantitatively with the aid of a densitometer[79], which made it possible to obtain the distribution of the linear and branched components in the PS specimen, illustrated in Fig. 19.[78] In conformity with the $R_f(\gamma)$ relation, these PS components were identified as branched (components 1 and 2), weakly branched (component 3), and linear (components 4 and 5). Assuming that the PS components form a continuous series ranging from linear to strongly branched, it was possible to conclude that the fifth component is true linear PS, while the fourth, third, second, and first components are respectively branched PS with one, two, three, and four units. It is now possible to employ the familiar relation[80] between R_s and the molecular weights of branched polymers, which is of the following form for PS: $R_s = 0.255\, hM^{1/2}$, where h is the branching factor and M the molecular weight. Since the PS investigated were synthesised with polystyryl-lithium as the initiator, they should have a comb-like structure. The corresponding values of h were selected for this model[81], which made it possible to obtain the molecular weights of the main and side chains of this branched polymer. Table 1[79] presents the results of a similar analysis of one of the PS specimens. It is noteworthy that 2 mg of the polymer was sufficient for such detailed analysis of the narrowly disperse PS specimen (with $M_w/M_n < 1.1$). The molecular weights of linear (found with the aid of TLC and PGC) and branched specimens and their branching parameters were determined, and component 5, whose content in the specimen analysed was 1–4%, was characterised.

Table 1. Results of the analysis of a polystyrene specimen (comb-like model).

Parameters	Component				
	branched			linear	
	1	2	3	4	5
R_s, A	20.5	21.5	32.5	22.5	16.5
MW of polymer	10 500	10 600	19 500	10 500	5500
MW of backbone	5 000	5 000	—	—	—
MW of branch	1 400	1 900	—	—	—
Content of component, %	23	15	16	42	4

2. Determination of the Polydispersity of Styrene–Methyl Methacrylate Block Copolymers with the Aid of Gel-Permeation, Thin-Layer, and Pyrolytic Gas Chromatography

The determination of the polydispersity of block copolymers includes the analysis of the distribution of their molecular weights, compositions, and admixtures of the corresponding homopolymers. It has been shown[33] that the polydispersity of block copolymers can be effectively studied with the aid of a combination of chromatographic methods with the following sequence of chromatographic operations. After the preliminary fractionation of the macromolecules in terms of size (by the GPC method), the fractions obtained are again chromatographed (this time by TLC), with respect to composition, and the block copolymer is separated from the admixture of homopolymers; finally, using PGC,[78] the compositions of the fractions obtained by the GPC and TLC methods are determined. The above procedure was used to investigate a block copolymer of the ABA type (where A = PMMA and B = PS).

The PGC method makes it possible to determine to within 1–2% the overall compositions of fractions containing the ST and MMA polymers, regardless of their molecular weight and chemical structure. The amount of specimens sufficient for analysis is 0.1–5 μg, and the method can therefore be used both for the analysis of the GPC fractions and the fractions separated with the aid of TLC. Interesting possibilities arise from a comparison of the compositions of the complete fraction and its separated components. It is easily shown that, when the compositions of two fractions, obtained with the aid of TLC, namely $x = m_1'/m_2'$ and $y = m_1''/m_2''$, and of the initial fraction (obtained by GPC), namely $z = m_1'''/m_2'''$, are known, then the ratio of the components separated by TLC ($\omega = q_1/q_2$) may be determined by the equation

$$\omega = \frac{(z-x)(1+y)}{(1+x)(y-z)}\,. \tag{22}$$

The block copolymer analysed was fractionated with the aid of GPC[33] in DMF on styrogel columns calibrated with respect to the R_S, and PMMA was fractionated simultaneously on similar columns. The fractions were analysed by PTLC in the chloroform-methanol system containing 80–72% of methanol as a function of R_S of the GPC fraction analysed (the molecular weight of PMMA). In this system PMMA moved along the plate, while the block copolymer remained at the start. Analysis of the GPC and TLC fractions by PGC made it possible to calculate by Eqn.(22) the content of the block copolymer in each fraction and, knowing the composition of the fraction and the increments in the refractive indices for PS and PMMA, to obtain (taking into account the additivity of the refractive indices in the copolymer solution[82]) the distribution in the block copolymer specimen analysed of the PS and PMMA components and the composition of the block copolymer as a function of R_S, as shown in Fig. 20.[33]

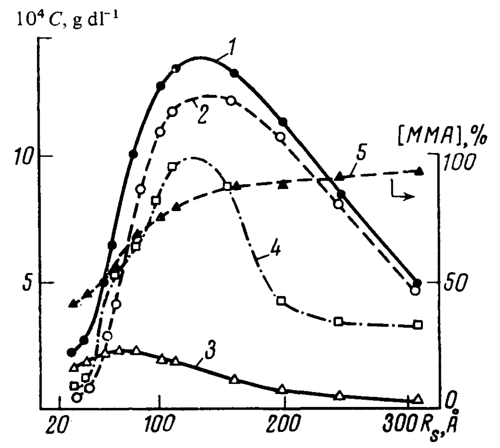

Figure 20. Distribution of PMMA–PS–PMMA block copolymers and PS and PMMA homopolymers as a function of R_S according to GPC, TLC, and PGC data: 1) initial polymer; 2) PMMA; 3) PS; 4) block copolymer; 5) PMMA content in block copolymer.

An interesting application of the combination of the two-detector (refractometer, spectrophotometer) GPC of an ST–BD block copolymer (with the simultaneous determination of its molecular weight distribution and compositions) and TLC for the investigation of the sequence of blocks in the copolymer has been demonstrated[83]. Since TLC established that the entire copolymer is of the three-block type, it was concluded that its bimodal distribution in GPC is associated with the presence of two types of three-block copolymers having different molecular weights.

3. Investigations of Graft Cellulose Copolymers with the Aid of Gel-Permeation and Thin-Layer Chromatography

In the study of gel copolymers it is usually necessary to establish whether the corresponding free homopolymers are present. TLC may be used for this purpose, as shown in relation to a PS–PMMA graft copolymer[3]. Another type of study of graft cellulose copolymers is based on the disruption of the cellulose base by acid hydrolysis or acetolysis and the determination of the molecular characteristics of the liberated graft homopolymer. However, difficulties are encountered here in the separation of the graft homopolymer and the homopolymer present as an admixture in the copolymer. A version of this method, proposed[84] for the study of a cellulose–styrene graft copolymer, consists in the acid hydrolysis of the copolymer, the separation of the free and grafted PS by adsorption TLC, and the determination of the molecular weight distribution of its PS by GPC. The polystyrene chains split off in the acid hydrolysis of the graft copolymer contain polysaccharide units at their ends, which exhibit a high adsorption activity. This, at first sight striking, high sensitivity of ATLC to the terminal glucosidic group of PS with $M = 10^5$ is co-related with the observed[36] sensitivity of ATLC in the separation of PS with $M = 5 \times 10^4 - 10^5$ and different numbers of terminal carboxy-groups.

Table 2. Results of the GPC analysis of polystyrene in the copolymer obtained by grafting PS on cellulose.

Specimen	$10^{-5}M_n$	$10^{-5}M_w$	M_w/M_n
PS after hydrolysis—PS_{tot}	2.8	13.0	4.65
Grafted PS—PS_{gr} (lower spot in TLC)	1.9	5.8	3.0
Free PS–PS_{fr} (upper spot in TLC)	4.9	17.0	3.5

Thus the free and grafted PS may be separated with the aid of ATLC on silica gel plates using THF as the eluent. The lower (starting) spot consists of grafted PS and the zone moving with the solvent front is free PS. If the chromatogram is developed by gradual spraying with a saturated solution of Thymol Blue in 50% aqueous ethanol and 3 N H_2SO_4, then the intensity of the blackening of the upper and lower spots makes it possible to determine the fraction of grafted PS (P_g) in the total amount of PS. Polystyrene was extracted from the plate with the aid of THF and its molecular weight distribution was determined by GPC on styrogel columns in THF. The observed values of M_w and M_n are listed in Table 2.[71] These data make it possible to determine the frequency index of the graft (F_g)—the ratio of the average number of polystyrene chains to the average number of cellulose chains in the graft copolymer: $F_g = [AP_g/M_n.(PS_{tot})][100/M_n\ (\text{cellulose})]$, where A is the increase in the weight of cellulose after PS has been grafted (expressed as a percentage)[71].

oOo

The thin-layer chromatography of polymers is a universal method for the study of the polydispersity of polymers and the diagnosis of different types of regularity and stereoregularity. This method combines all the useful features of TLC: simple apparatus, high sensitivity and speed of analysis, and comparative ease of selection of separating systems. At the same time the TLC of polymers also suffers from limitations: a relatively low reproducibility and the necessity to use in many instances reference polymer specimens (which may be obtained and characterised with the aid of GPC): however, the high sensitivity of TLC results in an economical use of such reference specimens.

Further progress in the TLC of polymers will involve the standardisation of analytical methods, in the first place quantitative methods, and the extension of the applications of this method to new classes of polymers and types of polydispersity. There is no doubt that the present development of the TLC method permits its effective employment both in the study of new polymers and in the industrial control of manufactured polymeric materials.

IX. APPENDIX

Table I. The use of adsorption chromatography in the study of polymers (on silica gel as the adsorbent). The following notation has been adopted: (MWD) = quantitative determination of MWD; (IC) = quantitative determination of inhomogeneity with respect to composition; an arrow represents the eluent gradient.

Polymer	Polydispersity investigated	Eluent	Method of development*	Refs.
	Homopolymers			
PMMA	w.r.t. MW (2×10^3 – 1.5×10^6)	chloroform + acetone (12:3.7)	1	101
PMMA	w.r.t. stereoregularity (separation of *a*- and *s*-PMMA from *i*-PMMA)	ethyl acetate	2	40
PMMA	Separation of the stereocomplex of *i*- and *s*-PMMA from *i*- and *s*-PMMA	acetone	2	41, 85
PMMA	Separation of *s*- and *a*-PMMA and w.r.t. MW (2×10^5–1.2×10^6)	isopropyl acetate + ethyl acetate (8:25)	2	15
PB	Separation of *trans*-1,4- and 1,2-vinyl-PB from *cis*-1,4-PB	carbon tetrachloride	3	43
PI	Separation of *trans*-1,4- and 3,4-vinyl-PI from *cis*-1,4-PI	cyclohexane + *p*-xylene (20:80)	3	44
PI	Separation of 3,4-vinyl-PI from *cis*-1,4-PI and *trans*-1,4-PI	carbon tetrachloride – *p*-xylene	3	44
PS	w.r.t. MW (from 314 to 2×10^6)	cyclohexane + benzene + acetone (40:16:0.4–2)	1	3, 13
PS	Separation of linear and branched polymers	cyclohexane + benzene + + acetone (40:16:0.4–1.5)	1	78
PS	Separation of 4-pointed star from linear polymer	cyclohexane + benzene (50:50) (25:75)	4	44, 86
PEO	w.r.t. MW (3×10^2– 2×10^4)	water + pyridine (9:1), THF	5	101
	Statistical copolymers (co)			
Poly(ST-co-MA)	w.r.t. composition (IC) (9.98–76% ST)	carbon tetrachloride + methylacetate (5:1) → methyl acetate	2	2
Poly(ST-co-MA)	w.r.t. composition (9.98–76% ST)	chloroform → ethyl acetate	2	2
Poly(ST-co-MMA)	w.r.t. composition (22–80% ST)	chloroform, dichloroethane, chlorobenzene + ethyl ether, EMK, acetone, dioxan, THF	1	1,3,7
Poly(ST-co-MMA) (azeotropic)	w.r.t. composition (54% ST)	chloroform + ethyl ether (12:4.2)	1	3,7
Poly(ST-co-MA)	Separation of statistical, alternating, and block copolymers	carbon tetrachloride + methyl acetate (5:1) → methyl acetate	2	12
Poly(ST-co-MMA)	Separation of statistical, alternating, and block copolymers	chloroform + ethyl acetate (25:5) → ethyl acetate, chloroform → ethyl acetate	2	12
Poly(ST-co-AN)	w.r.t. composition (15–31.2% AN)	chloroform + methyl acetate	2	87,88
Poly(ST-co-AN)	w.r.t. composition (IC) (up to 60% AN)	dichloroethylene → ethyl acetate	2	44
Poly(ST-co-AN)	w.r.t. composition (18.7–50.7% AN)	benzene, toluene → acetone	2	89,90
Poly(ST-co-BD)	w.r.t. composition (5–60% ST)	cyclohexane + benzene	4	91
Poly(ST-co-BD)	w.r.t. composition (IC) (14.6–62.4% ST)	carbon tetrachloride → chloroform + carbon tetrachloride (20:50)	4	30
Poly(ST-co-Bd)	Separation of statistical, alternating, and block copolymers	cyclohexane + chloroform (9:1) → chloroform, cyclohexane + chloroform (140:75)	4	11
Cellulose acetate	w.r.t. composition (IC) (52.5–60.5% CA)	dichloromethane + methanol (85:15)	6	92
Cellulose nitrate	w.r.t. composition (IC)	acetone + ethyl acetate (20:3) → chloroform + ethyl acetate (1:2)	6	93
Poly(ω-aminocapron. λ-co-aminolauryls)	w.r.t. composition	formic acid, formic acid + phenol	8	93
	Block copolymers			
Poly(ST-block-MMA)	w.r.t. composition (IC) (13.5–80.5% ST)	carbon tetrachloride → EMK	2	45
Poly(ST-block-MMA)	w.r.t. MW (68×10^3) and w.r.t. composition (9.1–53.7% ST)	nitroethane → acetone, carbon tetrachloride → methyl acetate, benzene → EMK	2	32
Poly(ST-block-MMA)	Block sequence (AB and ABA)	carbon tetrachloride + EMK**	2	45
Poly(ST-block-MMA)	Separation of PS, separation of block copolymer from PMMA	chloroform, benzene + EMK	4	84
Poly(ST-block-BD)	Block sequence (AB and ABA)	cyclohexane + chloroform (9:1) → chloroform	2	11
Poly(ST-block-BD)	Separation of statistical, two-block, and three-block copolymers	cyclohexane + chloroform (140:75)	4	84
Poly(ST-block-BD)	Separation of two-block copolymers from three-block copolymers	carbon tetrachloride***	4	84
Poly(ST-block-BD)	Separation of two-block and three-block copolymers	carbon tetrachloride + n-hexane*** (9:1)	4	84
Poly(ST-block-EO)	Separation of PS	cyclohexane + benzene + acetone (12:4:2)	1,5	3,7
" "	Separation of PEO	pyridine + water (3:7)	1,5	3,7
	Graft copolymers (gr)			
Poly(MMA-gr-ST)	Separation of PMMA and PS	acetone + acetic acid (12:2)	1	3,7
" "	Separation of PMMA and PS	chloroform + EMK (12:2)	1	3,7
" "	Separation of graft copolymer and PS from PMMA	cyclohexane + benzene + acetone (12:4:0.7)	1	3,7
" "	Separation of PS and PMMA from graft copolymer	acetone + acetic acid (12:2)	1	3,7
Poly(cellulose-gr-ST)	Separation of PS	THF, benzene	4	84
Poly(CTA-gr-ST)	Separation of CTA	dichloromethane + methanol (1:1), chloroform + dioxan (3:1)	7	47
" "	Separation of PS	chloroform	7	47
Poly(PVA-gr-ST)	Separation of PVA	methanol + water (9:1)	7	47
" "	Separation of PS	chloroform	7	47
Poly(PVA-gr-MMA)	Separation of PVA	methanol + water (9:1)	8	47
" "	Separation of PMMA	EMK + carbon tetrachloride (8:2)	8	47
Poly(nylon-gr-ST)	Separation of nylon	formic acid	8	47
" "	Separation of PS	chloroform	8	47
Poly(ETP-gr-ST)	Separation of PETP	phenol + water (75:25)	9	47
" "	Separation of PS	chloroform	9	47

Table I (cont'd.).

Polymer	Polydispersity investigated	Eluent	Method of development	Refs.
Poly(cellulose-gr-ST)	Separation of PS and graft PS	THF	4	71,84
Poly(BD-gr-ST)	Separation of PS and (PS-block-BD) copolymer	carbon tetrachloride + chloroform	4	44

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*Methods of development: 1) 3% $KMnO_4$ in concentrated H_2SO_4, with subsequent heating to 180°C; 2) 1% I_2 in methanol; 3) 14.7% H_2SO_4, with subsequent heating to 100°C; 4) saturated solution of Thymol Blue in 1 : 1 ethanol-water mixture, with subsequent spraying with 3 N H_2SO_4; 5) Dragendorff reagent; 6) 10% H_2SO_4, with subsequent heating to 110°C; 7) 10% $HClO_4$; 8) 0.05 N I_2; 9) Kayalon Fast Brown R solution in water-methanol mixture.

**The ratio depends on the composition of the block copolymer.

***Adsorbent— Al_2O_3.

Table II. The use of precipitation TLC in the study of polymers* (adsorbent-silica gel).

Polymer	Polydispersity investigated	Eluent	Method of development	Refs.
	Homopolymers			
PS	w.r.t. MW (1.98×10^4–5.1×10^4)	chloroform + acetone (10:1) → chloroform	4	44,86
PS	w.r.t MW (10^4–2×10^4)	acetone	10***	31
PS	w.r.t. MW (10^4–1.6×10^5)	acetone + chloroform	10	31
PS	w.r.t. MW (10^4–10^6)	acetone → acetone + chloroform (95:5–70:30)	10	31
PS	Ditto	acetone → acetone + THF (95:5–70:30)	10	31
PS	"	acetone → acetone + toluene (95:5–70:30)	10	31
PS	w.r.t. MW (10^4–10^6)	benzene + isopropyl alcohol (64.2–35.8)	10	16
PS	w.r.t. MW (10^4–10^6), (MWD)	dioxan + methanol (71.4 : 28.6) (θ)	7	16
PS	w.r.t. MW (10^4–10^6) (MWD)	acetone + isopropyl alcohol (96 : 4) → acetone + chloroform + isopropyl alcohol (66 : 30 : 4)	7	16
PS	w.r.t. MW (2×10^4–8.6×10^5)	dioxan + isopropyl alcohol (55:45)	10	19
PS	w.r.t. MW (MWD)	acetone + benzene + ethanol (3 : 1 : 2), benzene + EMK (1 : 1)	4	71
PS	w.r.t. MW (2×10^3–5×10^5)	benzene + EMK + acetone + ethanol (5 : 3 : 6 : 4)	4	71
PS	Separation of *i*-PST from *a*-PST	cyclohexane + benzene + acetone (40 : 16 : 2)	1	101
PS	Separation of 4-pointed star from PS with MW = 10^5–10^6	chloroform + acetone (10:1), chloroform	4	44,86
PS	Separation w.r.t. MW of polymers with terminal COOH groups (1.1×10^4–5×10^4 and 2.3×10^4–1.2×10^5)	THF + acetone (10:1) → THF	4	
PMMA	w.r.t. MW (4×10^4–4×10^5)	chloroform + methanol (29 : 71)	2	
PMMA	w.r.t MW (1.6×10^5–4.12×10^5)	benzene + acetone (2 : 8), isopropyl alcohol + methyl acetate (100 : 62), ethyl acetate + methyl acetate (100 : 23)	2	
PMMA	Separation of *s*- and *a*-PMMA and w.r.t. MW	acetonitrile + methanol (20 : 40, 46 : 54)	2	
PEO	w.r.t. MW (1.5×10^3–6×10^3)	ethylene glycol + methanol (80 : 20)	2	15
PEO	w.r.t. MW (1.5×10^3–2.8×10^4)	methanol → methanol + DMF (80 : 20)	2	31
PB	Separation of *cis*-1,4- and 1,2-PB from *trans*-1,4-PB	pentyl chloride	3	43

Table II (cont'd.).

Polymer	Polydispersity investigated	Eluent	Method of development	Refs.
	Copolymers (co)			
Poly(ST-co-BD)	w.r.t. MW (6.1×10^4–1.4×10^5)	THF → methanol	4	84
Poly(ST-block-MMA)	Separation of PMMA	chloroform + methanol (6 : 16–4 : 16)	1	33
Poly(ST-block-BD)	Separation w.r.t. MW, separation of low-molecular-weight PS	chloroform + methanol (3 : 2) → methanol	3	84
Poly(BD-gr-ST)	Separation of PS	EMK	3	44

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*For the methods of development and the significance of abbreviations, see Table I of the Appendix.

**Adsorbent— Al_2O_3.

***Method of development— $ZnSiO_3$.

Table III. The use of TLC in the study of oligomers* (adsorbent– silica gel).

Oligomer	Polydispersity investigated	Eluent	Method of development	Refs.
Polyisoprene	w.r.t. MW (700–2100), M_n = 1780	benzene + acetone (17.43 : 28.57)**	1	64
Polybutene	w.r.t. MW, M_n = 300	hexane	2	102
Poly-1,2-butadiene	w.r.t. functionality (COOH and OH groups)	*p*-xylene, carbon tetrachloride + THF (100 : 1)	3	44
	Non-functional, mono- and bi-functional	cyclohexane + benzene (14 : 3)	4	67
PS	w.r.t. MW (n = 3–9), M_n = 900	carbon tetrachloride + heptane (2 : 1)	4	67
Poly-α-methylstyrene	w.r.t. MW (n = 3–10)	ethyl acetate + isopropyl alcohol + acetone + methanol + water (50 : 15 : 15 : 4 : 16), isopropyl alcohol + ethyl acetate + water*** (30.5 : 55 : 14.5)	5	56
Polyglycerols	(1) w.r.t. MW (n = 1–4) (2) separation of linear and branched oligomers			
PEG	w.r.t. MW (n = 1–3) (M_n = 200–2000)	chloroform + ethanol (92 : 8)***	1	50
PEG (3,5-dinitrobenzoates)	w.r.t. MW (M_n = 200–2800)	EMK sat. with water	6	51
PEG (dichloro-derivatives)	w.r.t. MW (up to n = 21)	EMK sat. with water	1	94
PEG (dichloro-derivatives, triphenylmethyl derivatives)	w.r.t. MW (n = 13.2) (n = 17.2)	EMK sat. with water	1	95
PEG (3,5-dinitrobenzoates	w.r.t. MW (M_n = 200–4000) (MWD)	EMK sat. with water	7	53
PEG	w.r.t. MW (M_n = 600)	pyridine + water (0.1 : 10), chloroform + ethanol (10 : 1)*****	6	67
PPG	w.r.t. functionality	hexane + di-isopropyl ether + ethanol + water (5 : 10 : 5 : 3)	8	61
PPG	w.r.t. MW (M_n = 150–2000)	ethyl acetate + acetic acid (97.5 : 2.5)	1,9, 10	53
PPG	w.r.t. functionality (monools, diols, triols, and pentols) M_n = 500–5000)	ethyl acetate sat. with water	6	48
Mixture of PPG and PEG	Separation	chloroform + white spirit (85 : 15)	7	53
Mixture of PPG, PEG, and poly-THF	Separation (M_n = 2000)	chloroform + ethanol (92 : 8)	1	50
PEG–nonyl ether	w.r.t. MW (n = 9)	EMK sat. with water	11	59
PEG and its derivatives ($-O-CH_2CH_2SR$, where R = phenyl, n-hexyl, n-octyl, or n-decyl; $-O-CH_2CH_2Cl$ and $-OR$, where R = phenyl or triphenylmethyl)	w.r.t. MW (up to n = 13)	EMK and EMK sat. with water	1	57

Table III (cont'd.)

Oligomer	Polydispersity investigated	Eluent	Method of development	Refs.
PEG and its derivatives R–O(CH_2CH_2O)$_n$R', where R = R' = H, R = R' = phenyl, or R = *p*-t-nonylphenyl and R' = H	w.r.t. MW (up to *n* = 17) *n* = 6.5 *n* = 7.3 *n* = 5.4	EMK, EMK + water (9:1); EMK + water (95:5); EMK sat. with water	1	2
PEG–*p*-t-nonyl phenyl ether	w.r.t. MW (*n* = 6.5–12.9)	EMK sat. with water	1	60
Surfactants based on PEG	w.r.t. MW (up to *n* = 8.6)	EMK sat. with water	1	96
Surfactants based on PEG of the type RO(CH_2CH_2.O)$_n$, where R = alkylphenyl or alkyl	w.r.t. MW	EMK sat. with water	1	97
Products of condensation of PEG with aliphatic acids, alcohols, amines, phenols, and amides	w.r.t. MW and degree of hydroxyethylation (up to 1:20)	EMK + water (1:1)—upper phase, EMK + 2.5% aqueous ammonia (1:1)—upper phase, butanol + acetic acid + water (4:1:5)	6	49
Esters of PEG and adipic acid	Separation of linear and branched oligomers (M_n = 1000–3000)	benzene + ethanol (3:1)		
Poly(methylene-2-hydroxybenzoate)	w.r.t. MW (138–1100)	benzene + acetic acid + water (2:2:1)	12	98
ε-Caprolactam and its cyclic oligomers	w.r.t. MW (*n* = 1–8)	THF + petroleum ether (100–120°C) + water (80:14:10); 1-butanol + acetic acid + water (10:2:5); 2-butanol + formic acid + water (7.5:1.5:1); 1-butanol sat. with water; isopropyl alcohol + methanol + water (1:1:1); 1-butanol + conc. HCl + water (10.2:3.8)	6	65
Poly(ethylene terephthalates)	Separation w.r.t. functionality	benzene + ethyl acetate (85:15, 55:45) → ethyl acetate	13	63
Diethylene glycol in poly(ethylene terephthalate)		Dichloromethane + 25% aqueous ammonia + methanol (8:3:17)	14	100
Polydimethylsiloxanediols	w.r.t. MW (*n* = 1–20)	benzene + ethyl acetate (10:0.1)	15	67

Methods of development: 1) I_2 vapour; 2) 1% vanillin and 10% $HClO_4$ with subsequent heating at 110°C for 1 h; 3) 14.7% H_2SO_4 with subsequent heating to 100°C; 4) 3% $KMnO_4$ in concentrated H_2SO_4 with subsequent heating to 180°C; 5) 0.5% Thymol Blue in 95:5 ethanol–H_2SO_4 mixture with subsequent heating at 120°C for 1 h; 6) Dragendorff reagent; 7) acetic acid solution of $KMnO_4$; 8) cobalt thiocyanate; 9) 0.05% ethanol solution of rhodamine B; 10) 2% $KMnO_4$ in 2 *N* H_2SO_4; 11) 1% I_2 in methanol; 12) u.v. irradiation at 366 nm; 13) Methyl Red, Bromothymol Blue, and formaldehyde in 95% ethanol; 14) 0.5% $KMnO_4$ and $K_2S_2O_8$; 15) luminescence of background at 365 nm.

*For the notation employed, see Table I.

**Al_2O_3 (17% of water), neutral unfixed layer.

***Mixture of kieselguhr and silica gel.

****Al_2O_3 with first degree of activity, unfixed layer.

*****Adsorbent—Al_2O_3.

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REVIEWS
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The Problems of the Selectivity of Chemical Reactions

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The review discusses the problem of the selectivity of chemical processes of different classes. Mathematical expressions are given for the selectivity of reactions of simple types and for radical-chain processes and a relation is demonstrated between the selectivity and the kinetic parameters of the reaction. Factors controlling the selectivity by influencing the mechanism of the process and its kinetics are considered—chemical and physical factors (catalysing, inhibiting, and complex-forming additives, factors associated with control of the reaction by carrying it out at low temperatures, by employing laser radiation and magnetic and electric fields, etc.).
Data on reaction selectivity and ways of improving it are considered in relation to specific examples of oxidation, polymerisation, cracking, and halogenation reactions involving organic substances.
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I. INTRODUCTION

The problem of the effective utilisation of natural raw materials is of fundamental importance in modern chemistry. The high selectivity and rate of a chemical reaction involving a low expenditure of energy and apparatus of minimum size have become the main criteria of the practical usefulness of a chemical process. The solution of the problem of the optimisation of a process presupposes the knowledge of the kinetic parameters and mechanism of the given chemical reaction, i.e. the chemical kinetics. Thus chemical kinetics have become the scientific basis of chemical engineering.

This review is devoted to the problem of the selectivity of simple and complex (including a large number of elementary stages) chemical reactions and the physicochemical and kinetic factors which determine the selectivity.

II. SELECTIVITY, CONVERSION, AND REACTION YIELD

The concept of the "quantitative yield" of the reaction product, which is frequently employed, corresponds to the idea of a high process selectivity. However, the quantitative definition of the term "selectivity" must be more rigorous, particularly in view of the fact that different definitions are stated in the literature.

The integral selectivity S_P (with respect to the product P) of the reaction

$$\underset{\text{initial compounds}}{A, B, \ldots} \longrightarrow \underset{\text{intermediates}}{\pi_1, \pi_2 \ldots\ldots} \quad \underset{\text{final products}}{P, P_1 \ldots}$$

is defined by the relation

$$S_P(t) = \frac{f\Delta P}{\Delta A} = \varphi_P / C_A = \frac{f\int\limits_0^t w_P \, \mathrm{d}t}{\int\limits_0^t |w_A| \, \mathrm{d}t}, \tag{1}$$

where ΔP is the amount (or concentration when the volume is constant) of the product P formed, w_P the rate of its accumulation, ΔA the amount of unreacted initial substance A in relation to which the selectivity is determined, $|w_A|$ the absolute rate of consumption of A, f a normalising factor related to the stoichiometric coefficients of the chemical equation, $\varphi_P = f\Delta P/A_0 = \int_0^{f\Delta P} \mathrm{d}P/A_0$ the yield of the product P (A_0 is the initial amount of substance A), and $C_A = \Delta A/A_0$ the degree of conversion of substance A; the form of the function $w(t)$ is determined by the specific reaction mechanism.

Thus the selectivity characterises the fraction of the initial substance converted into the product P. It is a function of time and hence also of the degree of reaction, the rate constants for the elementary processes, and the concentrations of the substances involved in the reaction.

The relation between S and C, i.e. between the selectivity and the degree of conversion, can be formulated thus:

$$S(C) = \frac{f}{C_A}\int\limits_0^{\Delta P} \frac{\mathrm{d}P}{A_0} = -\frac{1}{C_A}\int\limits_0^{C_A} \frac{f\,\mathrm{d}P}{\mathrm{d}A}\,\mathrm{d}C_A = \frac{1}{C_A}\int\limits_0^{C_A} \sigma\,\mathrm{d}C_A, \tag{2}$$

since $\mathrm{d}C_A = -\mathrm{d}A/A_0$, $C_A = 0$ when $A = A_0$, and the degree of conversion is equal to C_A when $A = A_0 - \Delta A$.

The quantity

$$\sigma = -\frac{f\,\mathrm{d}P}{\mathrm{d}A} = -\frac{f\,\mathrm{d}P/\mathrm{d}t}{\mathrm{d}A/\mathrm{d}t} = -\frac{fw_P}{w_A} \tag{2a}$$

is called the differential selectivity. In relation to reactions in flow systems, σ may be used as an independent selectivity criterion. For an ideal mixing reactor, Eqn. (2a) reduces to a formula analogous to Eqn. (1). In a flow system under steady-state conditions at constant volume of the reaction mixture, the following relations hold:

$$w_P = v_P\,[P]_{st},$$
$$w_A = v_0\,[A]_0 - v_A\,[A]_{st},$$

where v_0, v_A, and v_P are the specific rates of supply and removal of A and of removal of the product P respectively. We then have

$$\sigma = \frac{fw_P}{|w_A|} = \frac{fv_P\,[P]_{st}}{|v_0\,[A]_0 - v_A\,[A]_{st}|}\;; \tag{3}$$

where $v_0 = v_A = v_P$, we find

$$\sigma = f\,[P]_{st}/([A]_0 - [A]_{st}) = f\,[P]_{st}/(\Delta\,[A])_{st},$$

i.e. in the steady state the differential selectivity is identical with the integral selectivity.

In closed systems σ does not characterise the selectivity adequately and may actually become negative. In certain cases (heterogeneous catalytic processes) an integral selectivity criterion is used in the form

$$S' = \Delta P_i \Big/ \sum_{j\neq i} \Delta P_j = \int\limits_0^t w_{P_i}\,\mathrm{d}t \Big/ \int\limits_0^t \sum_{j\neq i} w_{P_j}\,\mathrm{d}t, \tag{1a}$$

where ΔP_i is the amount (concentration) of the product P_i and $\sum_{j\neq i} = \Delta P_j$ is the total amount of all the reaction products with the exception of P_i.

III. SELECTIVITY OF REACTIONS OF SIMPLE TYPES

In chemical kinetics the entire wide variety of chemical reactions reduce to a limited number of kinetic types: reactions of simple orders and simple consecutive, parallel, reversible, autocatalytic, and chain processes. Complex chain reactions are frequently described by simple kinetic laws, so that the problem of selectivity is considered primarily in relation to a set of first-order reactions occurring simultaneously.

1. Reaction of the type

$$A \xrightarrow{k} mP\ .$$

In this case

$$-\mathrm{d}\,[A]/\mathrm{d}t = f\mathrm{d}\,[P]/\mathrm{d}t,$$

i.e. $|w_A| = fw_P$, where $f = 1/m$, and, according to Eqns. (1) and (2), we have $S(t) = 1$ and $S(C) = 1$.

Thus the selectivity of simple chemical reactions taking place in one stage and leading to the formation of a single desired product only is always equal to unity throughout the chemical reaction (Fig. 1).

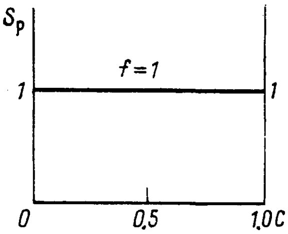
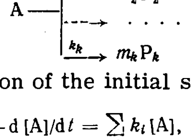


Figure 1. The selectivity in a simple irreversible reaction.

2. The parallel reactions



$$A \left\{ \begin{array}{l} \xrightarrow{k_1} m_1 P_1 \\ \xrightarrow{k_2} m_2 P_2 \\ \dashrightarrow \;\cdot\;\cdot\;\cdot\;\cdot \\ \xrightarrow{k_k} m_k P_k \end{array} \right.$$

The rate of consumption of the initial substance A is given by

$$-\mathrm{d}\,[A]/\mathrm{d}t = \sum_i k_i\,[A],$$

and the formula

$$\mathrm{d}[\mathrm{P}_j]/\mathrm{d}t = m_j k_j [\mathrm{A}].$$

expresses the rate of accumulation of P_j. Consequently

$$S_{\mathrm{P}_j}(t) = S_{\mathrm{P}_j}(C) = f_j k_j \Big/ \sum_i k_i = \text{const},$$

where $f_j = 1/m_j$. Evidently, the selectivities $S(C)$ and $S(t)$ of parallel first-order reactions are also independent of both the time and the degree of reaction (they remain constant throughout the reaction) and are determined by the stoichiometry of the reaction and the rate constants for the individual stages.

When the order n of even one of the parallel stages (l) is other than unity ($n \neq 1$), we have

$$-\mathrm{d}[\mathrm{A}]/\mathrm{d}t = \sum_{i\neq l} k_i [\mathrm{A}] + nk_l [\mathrm{A}]^n,$$

$$\mathrm{d}[\mathrm{P}_j]/\mathrm{d}t = m_j k_j [\mathrm{A}],\ \mathrm{d}[\mathrm{P}_l]/\mathrm{d}t = m_l k_l [\mathrm{A}]^n;$$

$$S_j(t) = \frac{f_j \int\limits_0^t k_j [\mathrm{A}]\,\mathrm{d}t}{\int\limits_0^t \Big(\sum\limits_{i\neq l} k_i [\mathrm{A}] + nk_l [\mathrm{A}]^n\Big)\,\mathrm{d}t} \quad (\text{for } j \neq l),$$

$$S_l(t) = \frac{f_l \int\limits_0^t k_l [\mathrm{A}]^n\,\mathrm{d}t}{\int\limits_0^t \Big(\sum\limits_{i\neq l} k_i [\mathrm{A}] + nk_l [\mathrm{A}]^n\Big)\,\mathrm{d}t},$$

where $f_j = 1/m_j$ and $f_l = n/m_l$.

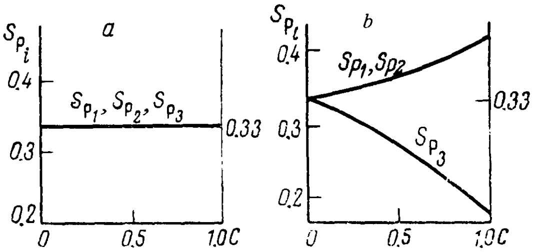


Figure 2. The selectivity in parallel reactions: *a*) three first-order reactions ($k_1 = k_2 = k_3$); *b*) two parallel first-order reactions and one second-order reaction $\{k_1 = k_2 = k_3[\mathrm{A}]_0\}$.

Although these equations can in fact be integrated, they lead to complex formulae, so that it is much more convenient to calculate the function $f_j(C)$. The expressions for differential selectivity required in these calculations are formulated as follows:

$$\sigma_{j(j\neq l)} = \frac{f_j k_j}{\sum\limits_{i\neq l} k_i + nk_l [\mathrm{A}]^{n-1}} = \frac{f_j k_j}{\sum\limits_{i\neq l} k_i + nk_l [\mathrm{A}]_0^{n-1} (1-C)^{n-1}} \tag{4}$$

for all the products formed in first-order reactions and

$$\sigma_l = \frac{f_l k_l}{\sum\limits_{i\neq l} k_i [\mathrm{A}]^{1-n} + nk_l} = \frac{f_l k_l}{\sum\limits_{i\neq l} k_i [\mathrm{A}]_0^{1-n} (1-C)^{1-n} + nk_l} \tag{5}$$

for the product formed in the nth order reaction.

It is seen from Figs. 4 and 5 that, as the initial substance A is consumed, the differential process selectivity with respect to any product changes monotonically. When $n > 1$, the quantity σ_j ($j \neq 1$) increases monotonically with the degree of reaction and σ_l diminishes monotonically; on the other hand, when $n < 1$, σ_j diminishes and σ_l increases. It follows from Eqn. (2) that, for the monotonic variation of the differential selectivity σ, the integral selectivity S varies in parallel with the latter. Accordingly, when $n > 1$, an increase in the degree of conversion entails an increase of S_j and a decrease of S_l, while under conditions where $n < 1$, the opposite situation obtains, i.e. S_j decreases and S_l increases (Fig. 2). For integral values of n, the expressions for the integral selectivities may also be obtained in terms of quadratures, for example, for $n = 2$ and $m_j = 1$, we have

$$S_j = \frac{k_j}{2k_l [\mathrm{A}]_0 C} \ln\left(1 - \frac{k_l [\mathrm{A}]_0 C}{\sum\limits_{i\neq l} k_i + 2k_l [\mathrm{A}]_0}\right);$$

$$S_l = 2\left\{1 + \frac{\sum\limits_{i\neq l} k_i}{2k_l [\mathrm{A}]_0 C} \ln\left(1 - \frac{2k_l [\mathrm{A}]_0 C}{\sum\limits_{i\neq l} k_i + 2k_l [\mathrm{A}]_0}\right)\right\}.$$

3. A sequence of first-order reactions:

$$\mathrm{A} \xrightarrow{k_1} m_1\pi_1 \equiv \pi_1 \xrightarrow{k_2} m_2\pi_2 \equiv \pi_2 \longrightarrow \cdots \equiv \pi_{k-1} \xrightarrow{k_k} m_k\mathrm{P}\,.$$

The system of differential equations for this process is of the form

$$\left.\begin{aligned} -\mathrm{d}[\mathrm{A}]/\mathrm{d}t &= k_1 [\mathrm{A}], \\ \mathrm{d}[\pi_1]/\mathrm{d}t &= m_1 k_1 [\mathrm{A}] - k_2 [\pi_1], \\ &\cdots\cdots\cdots\cdots\cdots \\ \mathrm{d}[\pi_{k-1}]/\mathrm{d}t &= m_{k-1} k_{k-1} [\pi_{k-2}] - k_k [\pi_{k-1}], \\ \mathrm{d}[\mathrm{P}]/\mathrm{d}t &= m_k k_k [\pi_{k-1}]. \end{aligned}\right\} \tag{6a}$$

Accordingly the differential selectivities are given by

$$\left.\begin{aligned} -\sigma_{\mathrm{P}_1} &= \frac{f_1\,\mathrm{d}[\pi_1]}{\mathrm{d}[\mathrm{A}]} = -1 + \frac{k_2}{m_1 k_1} \cdot \frac{[\pi_1]}{[\mathrm{A}]}, \\ &\cdots\cdots\cdots\cdots\cdots\cdots\cdots \\ -\sigma_{\mathrm{P}_{k-1}} &= \frac{f_k\,\mathrm{d}[\pi_{k-1}]}{\mathrm{d}[\mathrm{A}]} = \frac{f_{k-1} m_{k-1} (k_{k-1} [\pi_{k-2}] - k_k [\pi_{k-1}])}{k_1 [\mathrm{A}]}, \\ -\sigma_{\mathrm{P}_k} &= \frac{f_k\,\mathrm{d}[\mathrm{P}]}{\mathrm{d}[\mathrm{A}]} = \frac{f_k m_k k_k [\pi_{k-1}]}{k_1 [\mathrm{A}]}, \end{aligned}\right\} \tag{6}$$

where $f_k = 1 \Big/ \prod\limits_{i=1}^{k} m_i$.

By integrating Eqns. (6), it is possible to obtain an expression for the integral selectivity $S(C)$ corresponding to any product. The selectivity with respect to π_1

$$S_{\pi_1}(C) = m_1 \frac{(1-C)^{k_2/k_1} - (1-C)}{(1 - k_2/k_1)\,C} \tag{7}$$

decreases from 1 to 0 with increase of the degree of conversion (Fig. 3). For $k_2/k_1 < 2$, $S_{\pi_1}(C)$ changes relatively little up to high degrees of conversion [the plot of the function $S_{\pi_1}(C)$ has a convex region]. For $k_2/k_1 > 2$, $S_{\pi_1}(C)$ varies sharply under the conditions of low values of C [the function $S_{\pi_1}(C)$ is concave].

For selectivity with respect to π_2, we have

$$S_{\pi_2}(C) = \frac{m_1 m_2 k_1 k_2}{(k_2 - k_3)} \cdot \frac{1}{C} \left\{ \frac{(1-C)^{k_2/k_1}}{k_2 - k_1} - \frac{(1-C)^{k_3/k_1}}{k_3 - k_1} + \frac{(1-C)(k_2 - k_3)}{(k_2 - k_1)(k_3 - k_2)} \right\}.$$

When $t \to 0$ and $t \to \infty$, the function $S_{\pi_2}(C) \to 0$, so that the maximum selectivity with respect to π_2 is attained for an optimum degree of conversion of the initial substance (Fig. 3).

For all subsequent intermediates, S also passes through a maximum, but the formulae for selectivity become more cumbersome. Naturally the process selectivity with respect to any product is higher the lower the rate of its consumption. This is clearly seen from Eqns. (6): the lower the constant k_k the higher the value of $\sigma_{\pi_{k-1}}$ and hence also of $S_{\pi_{k-1}}(C)$.

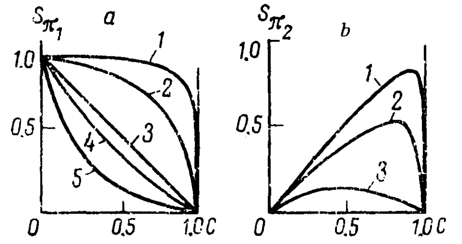


Figure 3. The selectivity in the formation of products in a first-order consecutive reaction $A \rightarrow \pi_1 \rightarrow \pi_2 \rightarrow P$: *a*) for the first intermediate and different rate constant ratios k_2/k_1 [1) 0.1; 2) 0.5; 3) 2; 4) 3; 5) 10]; *b*) for the second intermediate, $k_2/k_1 = 2$ and different k_3/k_1 ratios [1) 0.1; 2) 0.5; 3) 10].

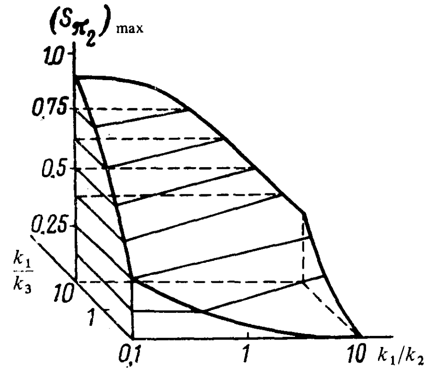


Figure 4. Selectivity with respect to the second intermediate in consecutive first-order reactions as a function of the ratio of the rate constants for individual stages.

A high selectivity with respect to an intermediate may be obtained if the rate constant for its consumption is significantly lower than the rate constant for its formation. Fig. 4 shows how the maximum process selectivity with respect to the second intermediate $(S_{\pi_2})_{\max}$ varies for different ratios of the rate constants k_1, k_2, and k_3. Evidently, the highest selectivities are attained when $k_1 \gg k_3 \ll k_2$. The selectivity with respect to the final product

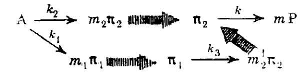
$$S_P(C) = 1 - \sum_{i=1}^{k-1} S_{\pi_i}$$

decreases monotonically with increase of C.

In order to achieve the transformation into the function $S(t)$, it is sufficient to use the time variation of the degree of conversion, i.e. the equation of the kinetic curve. In the case where the consumption of the initial substance follows first-order kinetics, the relation between C and t is

$$C = (1 - e^{-k_1 t}).$$

4. Consecutive-parallel reactions. The selectivity in the formation of any products of a complex consecutive-parallel reaction is determined by the stability of the reaction products and the probability that the reaction proceeds via different parallel pathways. For example, in the complex consecutive-parallel reaction



the differential process selectivity σ_1 with respect to the first product π_1 is determined by the factor associated with the parallel mechanism of the conversion of A into this product, namely $\alpha_{(A \rightarrow \pi_1)} = k_1/(k_1 + k_2)$, and the factor associated with the instability of the product π_1, namely $\beta_1 = k_3[\pi_1]/k_1[A]$, and can be formulated as follows:

$$\sigma_1 = \alpha(1 - \beta_1) = \alpha\gamma_1. \tag{8a}$$

The quantity $\gamma_1 = 1 - \beta_1$ characterises the accumulation of π_1 and may be called the accumulation factor.

The second product is formed via two pathways: directly from A and from the first intermediate π_1. The selectivity in the formation of π_2 is therefore determined by the sum of the selectivities in its formation via the two pathways. The selectivity in the formation of π_2 directly from A is determined from a formula analogous to Eqn.(8a):

$$\sigma_2(A \rightarrow \pi_2) = (1 - \alpha)\gamma_2 = (1 - \alpha)(1 - \beta_2),$$

where

$$\beta_2 = k[\pi_2]/(k_2[A] + k_3[\pi_1]),$$

The selectivity in the formation of π_2 via the second pathway, i.e. from π_1, is determined by the product of the factor associated with the parallel mechanism of the formation of π_1 from A (α), the π_1 instability factor (β_1), and the π_2 accumulation factor (γ_2):

$$\sigma_2(\pi_1 \rightarrow \pi_2) = \alpha\beta_1(1 - \beta_2) = \alpha\beta_1\gamma_2;$$

i.e.

$$\sigma_2 = \gamma_2(1 - \alpha + \alpha\beta_1). \tag{8b}$$

If the selectivity with respect to π_2 is proportional to the π_2 accumulation factor, then the selectivity with respect to the product P is proportional to the π_2 instability factor and is given by

$$\sigma = \beta_2(1 - \alpha + \alpha\beta_1). \tag{8c}$$

Eqns. (8a), (8b), and (8c) form a system of differential equations, the substitution of the solution of which in Eqn. (2) yields expressions for the integral selectivities with respect to all products.

The integral selectivity with respect to π_1 is described by a formula analogous to Eqn. (7):

$$S_{\pi_1}(C) = \alpha \frac{(1 - C)^{k_3/(k_1 - k_2)} - (1 - C)}{(1 - k_3/(k_1 + k_2))\,C} \tag{9}$$

and decreases from 1 to 0 with decrease in the degree of conversion, as for the product π_1 of the consecutive reaction (Fig. 5). The selectivity with respect to the product π_2 varies in accordance with the equation

$$S_{\pi_2}(C)=m_2\frac{k_1}{C}\left\{\frac{[k_2/k_1+k_3/(k_3-k_2-k_1)](1-C)}{k_1+k_2-k}+\right.$$
$$\left.+\frac{k_3}{(k_3-k_2-k_1)(k_3-k)}(1-C)^{k_3/(k_1+k_2)}+\frac{[k_2/k_1+k_3/(k_3-k)]}{k-k_2-k_1}(1-C)^{k/(k_1+k_2)}\right\}.$$

$S_{\pi_2}(C)$ may pass through a maximum for $k_2/k_1 < k_3/k$ (Fig. 5). Under these conditions, the product π_2 is formed predominantly owing to the conversion of π_1, i.e. is in essence the second intermediate in the sequence of transformations.

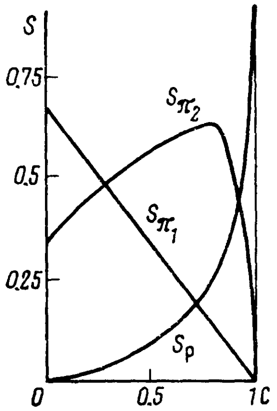


Figure 5. Selectivity in consecutive-parallel reactions. Calculation carried out for $k_1 = 2k_2$, $k = 1.5k_2$, and $k_3 = 6k_2$.

The selectivity with respect to the final product P_1 in this mechanism, as in any other sequence of reactions, increases with increased degree of conversion. Here the time variation of the degree of conversion

$$C=(1-e^{-(k_1+k_2)t})$$

makes it possible to transform the $S(C)$ relation into the expression for the time dependence of the selectivity in the formation of the products $S(t)$.

Expressions for the selectivities in the formation of products in a chemical process of any complexity may be obtained similarly.

IV. KINETIC ANALYSIS OF THE GENERAL SCHEME FOR A RADICAL-CHAIN REACTION AND SELECTIVITY

The kinetic mechanism of a chain process includes elementary steps of three types: (1) the formation of active centres propagating the chain; (2) chain propagation (steps involving the chain transformation of the substance, chain interconversion of the active chain-propagating centes), and (3) chain termination (destruction of active centres)[1-3]. If the chains are fairly long, then chain termination has almost no influence on the composition of the reaction products. The products formed during the process may interact with any active centres in the system, giving rise to secondary active species, whose reactivity as a rule differs from that of the primary species. Thus chain interaction assumes a significant importance.

The general mechanism of the radical-chain process can be represented in the following form when account is taken of the chain interaction mechanism (A) (see also Fig. 6).

Sources of free radicals:

$$\begin{array}{cccc} A, B, \dots\,; & \pi_j \Longrightarrow & r_0^{\cdot},\ r_j^{\cdot} \Longrightarrow & R_k^{\cdot} \\ \text{initial substances} & \text{intermediates} & \text{primary radicals} & \text{radical chain} \\ \text{(initiation)} & \text{(degenerate} & & \text{carriers} \\ & \text{branching)} & & \end{array}.$$

Chain formation:

$$A(B)\xrightarrow{k_0} r_i^{\cdot} \quad \text{(chain initiation)},$$
$$\pi_k \xrightarrow{k_{3k}} f\, r_k^{\cdot} \quad \text{(chain branching by the product } \pi_k\text{)},$$
$$A(B)+r_i^{\cdot}\xrightarrow{k_1} R_0^{\cdot}+P \quad \text{(formation of chain-propagating radical } R_0^{\cdot}\text{)}.$$

Chain propagation

$$\left.\begin{aligned} A+R_0^{\cdot} &\xrightarrow{k_{2.1}} \pi_1+R_0^{\cdot\prime} \\ B+R_0^{\cdot} &\xrightarrow{k_{2.2}} R_0^{\cdot} \end{aligned}\right\} \quad \text{(main chain in the conversion of the initial substance)}$$

$$\pi_i+R_i^{\cdot}\xrightarrow{k_2^{ii}} \pi_l+R_i^{\cdot} \quad \text{(secondary chain in the conversion of intermediates)}$$

$$\left.\begin{aligned} A+R_k^{\cdot} &\xrightarrow{k_{2.k}} \pi_s+R_0^{\cdot\prime} \\ \pi_j+R_0^{\cdot} &\xrightarrow{k_2^{0j}} \pi_1+R_j^{\cdot} \\ \pi_i+R_k^{\cdot} &\xrightarrow{k_2^{ki}} \pi_s+R_i^{\cdot} \end{aligned}\right\} \quad \text{(chain interaction)},$$

Chain termination

$$R_i^{\cdot}+R_j^{\cdot}\xrightarrow{k_{4.1}} P_{\text{term}} \quad \text{(quadratic chain termination in the interaction of active centres)}$$

$$R_i^{\cdot}\xrightarrow{k_{4.2}} P'_{\text{term}} \quad \text{(linear chain termination, for example in the interaction between a radical and the inhibitor).}$$

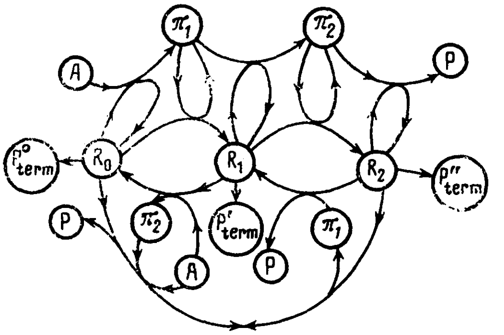


Figure 6. The pathways in a consecutive radical-chain reaction.

In this formulation the general mechanism for a chain reaction has a distinct structure, which emphasises the presence in the system of many sources of free radicals, distinguishes the units of the main and secondary chains and the interaction steps between the chains, and contains traditional types of elementary stages such as chain branching and termination†.

In examining the characteristics of a chain process use was made of fundamental concepts such as chain length ν and the rate of formation of radicals w_i in the chain initiation and branching stages. The length of the chain in the consumption of the initial substance A $[\nu_-^{(A)}]$ or in the consumption of any intermediate π_j $[\nu_-^{(\pi_j)}]$ is equal to the ratio of the rate of interaction of A or π_j with the free radicals to the rate of destruction of the latter, w_{term}. Since w_{term} in chain processes is usually equal to w_i, we have the following expressions for the chain lengths in the consumption process:

$$\nu_-^{(A)} = \left(\sum_i k_{2.i}\,[\dot{R}_i]\right)[A]/w_i,$$

$$\nu_-^{(\pi_j)} = \left(\sum_i k_2^{ij}\,[\dot{R}_i]\right)[\pi_j]/w_i, \tag{10}$$

where $k_{2.i}$ and k_2^{ij} are the rate constants for the interaction of the radicals with A and π_j. If the intermediate π_k is formed as a result of the interaction of an active centre $\dot{R}_l$ with any substance involved in the process, the chain length in the formation of π_k is proportional to the concentration of $\dot{R}_l$ and is determined by the relation

$$\nu_+^{(\pi_k)} = \left(\sum_i k_2^{li}\,[\pi_i]\right)[\dot{R}_l]/w_i, \tag{11}$$

where $\pi_0 = A$.

The chain lengths in the formation (ν_+) and consumption (ν_-) of the same substance are not identical and the difference between them characterises the change in the concentration of the substance during the process (the concentration of the latter increases and falls respectively when $\nu_+ > \nu_-$ and $\nu_+ < \nu_-$). The ratio of the rates of formation and consumption of the substances involved in the process is determined by the relative concentrations of the active centres in the system. For fairly long chains, the steady-state concentration of radicals is established as a result of their interconversion during the interaction between the chains. The rate of formation of the given radical in the chain is equal to the rate of its chain transformation:

$$\left(\sum_i k_2^{ij}\,[\dot{R}_i]\right)[\pi_j] = \left(\sum_i k_2^{ki}\,[\pi_i] + k_{2.k}\,[A]\right)[\dot{R}_k] \tag{12}$$

where π_j is the substance from which the active centre $\dot{R}_k$ is formed as a result of the interaction with the active centre $\dot{R}_i$.

Eqns.(12) constitute a system of algebraic linear homogeneous equations, whose number is equal to the number of types of radicals involved in the process. The rank of the coefficients matrix for this system of equations is smaller by unity than the number of equations. The relative concentration of any active centre can therefore be determined from Eqns.(12):

$$[\dot{R}_j] = \frac{D_{ij}}{D_i}\,[\dot{R}_i], \tag{13}$$

where D_i is the determinant corresponding to the coefficients matrix of Eqns.(13), from which the ith row and the ith column have been eliminated and D_{ij} is the determinant, analogous to D_i, obtained from the initial matrix by the transposition of the ith and jth columns.

On substituting Eqn.(13) into Eqns.(10) and (11) and then into Eqn.(2), we find an expression for the dependence of the process selectivity on the degree of conversion of the initial substance for a purely chain process when the contribution of molecular processes is insignificant:

$$S_{\pi_j} = \frac{1}{C}\int\limits_0^C \frac{\sum\limits_i (k_2^{ki}\,[\pi_i]\,D_{0k} - k_2^{kj} D_{0i}\,[\pi_j])\,\mathrm{d}C}{D_0 \sum\limits_i k_2^{0i}\,[\pi_i]}. \tag{14}$$

Eqn.(14) for the selectivity in the formation of any substance in an arbitrary chain process permits the following conclusions.

1. The selectivity is independent of the absolute concentration of the active centres in the system, i.e. of the rate of their formation (the integrand does not contain the absolute concentration of active centres).

2. Since the selectivity is independent of the absolute concentration of active centres, the factors which alter the rates of a chain process by altering the absolute concentration of active species (the effects of initiators and weak inhibitors) do not affect the process selectivity.

3. In the common instance where the reactivity of a radical in its reaction with molecules is independent of the nature of the radical and the rate constant for this reaction is determined solely by the properties of the molecules, the ratio

$$k_2^{ij}/k_2^{ik} = \varphi_{jk} = \text{const}$$

for the given j and k. The selectivity of a chain process of this kind is determined in the same way as the selectivity in a non-chain process proceeding via the same pathway without the participation of active centres. For a non-chain process, the ratios of the rate constants for the interconversion of the substance φ_{jk} are equal to the ratios of the rate constants for the interaction of the substances with the active centres in the chain process.

The selectivity of the chain process $S_{P_{term}}$ with respect to the product P_{term} formed in the chain initiation or termination step is a function of the chain length in the consumption of the initial substance:

$$S_{P_{term}} = \frac{n}{C}\int\limits_0^C \frac{\mathrm{d}C}{\nu_-^{(A)} + m}, \tag{15}$$

where n is the number of molecules of P_{term} formed in a single chain termination step and m the number of molecules of the initial substance consumed during the initiation and termination of a single chain. The maximum selectivity with respect to termination products is attained for the minimum chain lengths $[\nu_-^{(A)} = 1]$. For non-linear chain termination, the quantity $\nu_-^{(A)}$ is a function of the rate of initiation and the process selectivity depends in this instance on the rate of initiation.

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† In the text below the following numbering of the rate constants for individual elementary steps has been adopted: k_0 is the chain initiation rate constant, $k_{2.i}$ the rate constant for the ith reaction propagating the chain in the consumption of the initial substance, $k_{3.i}$ the rate constant for the ith chain branching reaction, and $k_{4.i}$ the rate constant for the ith chain termination reaction. The constants k_2^{ij} refer to secondary reaction chains; the first superscript refers to the reacting radical and the second to the given substance.

The absolute selectivity in the formation of P_{term} in a process with long chains is low, since the differential selectivity in the integrand of Eqns.(15) is inversely proportional to the chain length. At advanced stages of the reaction the chain length in the consumption of the initial substance diminishes owing to the decrease of the concentration of the latter. The integrand of Eqn.(15) then increases and there is a corresponding increase of the process selectivity with respect to the product P_{term}. For short chain lengths, the rate of initiation begins to influence also the process selectivity with respect to the products formed in the chain propagation reaction.

The case discussed above refers to processes where the formation and consumption of all the initial substances and reaction products take place only with participation of free radicals, (i.e. via a chain mechanism). When molecular reaction pathways or short chains occur, the characteristics of the variation of $S(C)$ and $S(t)$ change somewhat, in particular the process selectivity begins to depend on ν and w_i. A quantitative calculation of the selectivity of a chain process during which the chain length becomes small involves the solution of non-linear integrodifferential equations even in the simplest cases.

As an example of such a process, we shall consider a degenerate branched chain oxidation reaction where the hydrocarbon is consumed via a single pathway:

$$\begin{gathered}
\mathrm{ROOH} \xrightarrow{k_3} (\mathrm{RO^{\cdot}} + \mathrm{OH^{\cdot}}),\\
\mathrm{RO^{\cdot}} + \mathrm{RH} \xrightarrow{+\mathrm{O_2}} \mathrm{ROH} + \mathrm{RO_2^{\cdot}},\\
\mathrm{OH^{\cdot}} + \mathrm{RH} \xrightarrow{+\mathrm{O_2}} \mathrm{H_2O} + \mathrm{RO_2^{\cdot}},\\
\mathrm{RO_2^{\cdot}} + \mathrm{RH} \xrightarrow{k_2} \mathrm{ROOH} + \mathrm{RO_2^{\cdot}},\\
\mathrm{RO_2^{\cdot}} + \mathrm{RO_2^{\cdot}} \xrightarrow{k_4} \mathrm{R'{=}O} + \mathrm{ROH} + \mathrm{O_2}.
\end{gathered} \tag{B}$$

Application of the principle of the quasi-steady-state nature of the process with respect to the concentrations of the radicals $RO_2^{\cdot}$, $OH^{\cdot}$, and $RO^{\cdot}$, yields a system of differential equations describing the process kinetics:

$$\begin{gathered}
\mathrm{d}[\mathrm{ROOH}]/\mathrm{d}t = k_2[\mathrm{RO_2^{\cdot}}][\mathrm{RH}] - k_3[\mathrm{ROOH}],\\
\mathrm{d}[\mathrm{RH}]/\mathrm{d}t = k_2[\mathrm{RO_2^{\cdot}}][\mathrm{RH}] - fk_3[\mathrm{ROOH}],\\
[\mathrm{RO_2^{\cdot}}] = (fk_3[\mathrm{ROOH}]/k_4)^{1/2},
\end{gathered}$$

(f is the probability of the release of radicals into space during the hydroperoxide decomposition step) and hence the equation relating the concentration of the hydroperoxide and the hydrocarbon:

$$\frac{\mathrm{d}[\mathrm{ROOH}]}{\mathrm{d}[\mathrm{RH}]} = \frac{\nu - 1/f}{\nu + 1}, \tag{16}$$

where

$$\nu = \frac{k_2[\mathrm{RH}]}{(fk_3k_4[\mathrm{ROOH}])^{1/2}}.$$

The concentration of the hydroperoxide at any concentration of RH may be calculated by Eqn.(16) and the process selectivity may be determined for different degrees of conversion. The highest selectivity in a process of this kind is attained when $1 \ll \nu \gg 1/f$. Fig.7 presents the results of a numerical calculation of S_{RCOOH} for different values of the parameter $k_2[\mathrm{RH}]_0/(k_3k_4)^{1/2}$ ($f = 1$).

In this process the hydroperoxide is the first intermediate and, as in a usual consecutive reaction, the selectivity in its formation decreases monotonically with increased degree of conversion of the initial substance. However, in contrast to a non-chain process, the decrease of selectivity is not associated with the consumption of the hydroperoxide but with the decrease of the chain length in its formation caused by the increase of its concentration and by the corresponding increase of the rate of initiation. The form of the function $S_{ROOH}(C)$ is therefore independent of the rate constant for the decomposition of the hydroperoxide, but depends on the parameter determining the oxidation chain length $\{k_2[\mathrm{RH}]_0/(k_3k_4)^{1/2}\}$ and on the probability of the release of radicals into space during the hydroperoxide decomposition step (f). For this reason, the greatest change in selectivity for any values of the parameters occurs at the beginning of the process, for low degrees of conversion of RH, where the concentration of the hydroperoxide and the rate of initiation vary to the maximum extent.

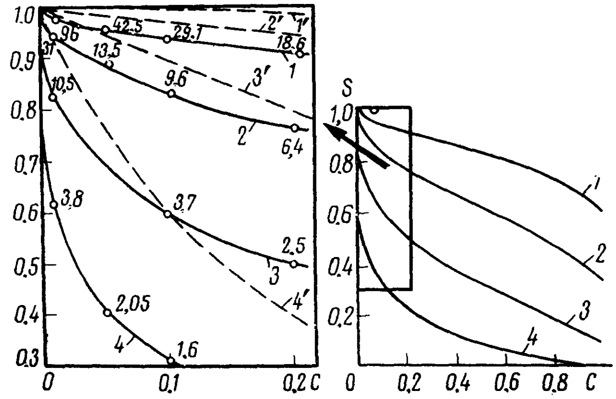


Figure 7. The selectivity in the formation of the hydroperoxide in a degenerate branched chain process as a function of the degree of conversion of the hydrocarbon oxidised for $f = 1$ and different values of the parameter $k_2[\mathrm{RH}]_0/(k_3k_4)^{1/2}$: 1) 10; 2) 3.16; 3) 1; 4) 0.316. The numerals opposite the calculated points denote the chain lengths under these conditions: 1')–4') the selectivities in the formation of the first intermediate in a simple consecutive reaction for the rate constant ratios k_2/k_1 = 0.1, 0.5, 2, and 10 respectively.

Fig. 7 presents the variation of the selectivity of the chain process discussed above and in a non-chain consecutive reaction (with the same sequence in the formation of products) for low degrees of conversion. In a consecutive reaction with low rate constants for the consumption of the first intermediate ($k_2/k_1 < 2$) the process selectivity corresponding to low degrees of conversion varies little and the function $S_{\pi_1}(C)$ is convex (Fig. 3). In a chain process the function $S_{ROOH}(C)$ is always concave for low degrees of conversion, i.e. $S_{ROOH}(C)$ changes sharply for low values of C. This form of the relation is due to the decrease of the chain length in the formation of the hydroperoxide owing to the increase of the rate of formation of active centres.

Thus kinetic analysis of the mechanism of a radical-chain process shows that the selectivity for the formation of chain propagation products in a reaction with long chains is independent of the rate of chain initiation and the absolute concentration of radicals. The characteristics of the variation of $S(C)$ are then largely analogous to those observed for the selectivity in a non-chain process proceeding via the same pathway. For short chains, S begins to depend on w_i and hence on ν. The selectivity in the formation of chain termination products P_{term} always depends on the rate of initiation (chain length) and assumes significant values only for fairly short chains.

V. FACTORS CONTROLLING SELECTIVITY

The best indication of the importance of chemical kinetics in experimental and practical research is the effective employment of kinetic parameters for controlling the rates and selectivities of chemical reactions.

For a long time the set of available factors capable of influencing a chemical reaction remained almost unchanged—the action of heat (heating, temperature rise), the influence of sunlight and chemical additives, and catalysis. Towards the end of the XXth century progress in science and engineering introduced into chemistry the action of ionising radiation, laser radiation, shock waves, the use of low temperatures (in contrast to the usual endeavour to increase the reaction temperatures), continuous processes, and modification and immobilisation of enzymes and cells as factors influencing the reaction. The principles of chemistry were given a profound and rigorous theoretical basis. This led to considerable possibilities in controlling chemical reactions, provided that their kinetics and mechanisms have been established, and to the possibility of altering the mechanism and kinetics when it is necessary and desirable from the scientific or technical point of view.

According to the formulae for selectivity, temperature as a rule influences the factors associated with a parallel-reaction mechanism (α) and the instability of the intermediate (β). Selective inhibition of undesirable and coupled processes leads to a change of α. In coupled processes these quantities depend on the relative activities of the radicals propagating the oxidation chain.

The introduction of complex forming agents (including solvents) also alters α and β owing to the decrease of the reactivity of the active centres. In certain cases (for short chains) the selectivity in a radical-chain processes depends on the chain length ν, which may be varied by the introduction of initiating additives or inhibitors which increase the rate of chain termination. The latter procedure is used in polymerisation, where a change in the viscosity and structural properties of the medium makes it possible to increase the molecular weight of the polymer and to alter the nature of the molecular weight distribution. The procedure involving the increased lifetime of the radical in the solid polymer led to the discovery of a new type of polymerisation—the radiation-induced graft polymerisation.

A new factor which increases selectivity is associated with the technique in which the reaction is carried out at low and ultralow temperatures (down to ~100 K) where many processes show high rates and high selectivities in the region corresponding to the transition of the system from the vitreous to the supercooled liquid state.

In the region of heterogeneous catalysis new possibilities arose in connection with the use of modified catalysts which propagate the process via a purely heterogeneous mechanism. A characteristic feature of such modified catalysts is the possibility of activating only one of the species involved in the chemical reaction (for example, O_2 in an oxidation process) and, conversely, a decrease of the ability of the catalyst to form complexes with other species (for example, the decreased rate of decomposition of the hydroperoxide in the autoxidation of hydrocarbons). In the presence of such catalysts the process selectivity is as a rule very high.

Homogeneous catalysis has become a fairly effective factor for influencing the selectivity in many chemical processes. The increase of the selectivity of radical-chain processes in the presence of homogeneous catalysts is associated with the selective acceleration of individual elementary stages.

Fundamentally new possibilities for increasing selectivity have arisen from the employment of catalysts which make it possible to propagate the process with participation of radicals bound in a complex with the catalyst (Lewis acids in polymerisation, dinuclear iron complexes in chlorination, etc.). In the presence of such catalysts reactions as a rule take place in the coordination sphere of the metal with a high selectivity.

Research based on the principles of the simulation of enzymatic systems has developed. The application of multicomponent homogeneous catalytic systems has led to many reactions which proceed with a selectivity which is actually higher than that in enzymatic processes.

The application of infrared laser chemistry has already given rise to instances where the reactivities and rates of conversion of individual substances were increased. These effects are used, in particular, for isotope enrichment. Thus under the influence of a HF laser, which emits coherent radiation in the region of 2.7 μm, CH_3OH molecules undergo selective excitation in a CH_3OH-CD_3OH mixture, and then become capable of reacting with Br_2 at high rates[4]:

$$CH_3OH + nh\nu \rightarrow CH_3OH^*,$$
$$CH_3OH^* + Br_2 \rightarrow \text{bromination products.}$$

By employing a 90 W HF laser, it is possible to enrich an equimolar CD_3OH-CH_3OH mixture to a 95% deuteromethanol content over a period of 1 min. Unfortunately laser chemistry has not as yet found applications in the solution of problems of increasing the selectivity in radical-chain processes to an extent which it merits.

Reactions in strong magnetic and electromagnetic fields will probably become common. The first examples of the use of magnetic and electric fields showed that the method is likely to be useful for increasing the selectivity in many chain processes.

The possibility of increasing the selectivity in chemical processes arising in connection with the employment of reactors where the reaction takes place under continuous conditions (ideal mixing and plug flow vessels) is beginning to attract much attention. Many reviews and monographs have been devoted to the simulation and optimisation of chemical reactors[5-7]. However, a fundamental deficiency of these studies is the employment of overall reaction mechanisms in the calculations, whereas knowledge and use in the calculations of specific chemical schemes for the elementary reaction rate constants might be very important. The importance of this approach becomes evident when account is taken of the fact that the method used to carry out the process may have a significant influence on the characteristics of the individual stages and hence the entire process. For example, a significant factor is that, by carrying out the reaction in an open system, one may promote the attainment of steady-state concentrations differing from those corresponding to thermodynamic equilibrium. Thus, for a simple reversible first-order reaction $A \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} P$ in an open system, the ratio of the steady-state concentrations of P and A is

$$\frac{[\mathrm{P}]_{\mathrm{st}}}{[\mathrm{A}]_{\mathrm{st}}}=\frac{k_1([\mathrm{A}]_0+[\mathrm{P}]_0)+v[\mathrm{P}]_0}{k_{-1}([\mathrm{A}]_0+[\mathrm{P}]_0)+v[\mathrm{A}]_0}\neq\frac{k_1}{k_{-1}},$$

where $[\mathrm{A}]_0$ and $[\mathrm{P}]_0$ are the concentrations of A and P in the solutions supplied to the vessel and v is the flow rate.

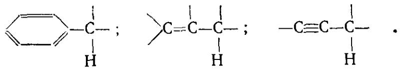
Thus analysis of specific chemical mechanisms plays in all cases an important role in the solution of problems associated with the optimisation of chemical processes. Certain specific examples of selective reactions and methods of increasing selectivity are considered below in relation to oxidation, polymerisation, cracking, and halogenation of organic substances.

VI. LIQUID-PHASE OXIDATION REACTIONS

Liquid-phase reactions involving the oxidation of organic substances are exceptionally widely used as objects of theoretical and experimental studies in the field of radical chain reactions and they are therefore important for chemical practice.

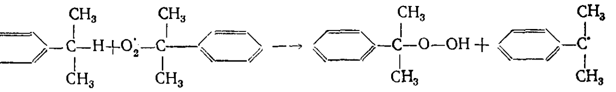
1. Dependence of Reaction Selectivity on Chain Length

A high selectivity in the formation of hydroperoxides at low temperatures is characteristic of the chain oxidation of aromatic alkyl derivatives, α-olefins, and other hydrocarbons with reactive C–H bonds activated by conjugation with an aromatic ring or with unsaturated carbon–carbon bonds:



In this case the process is a degenerate branched chain reaction proceeding via mechanism (B) (see Section IV).

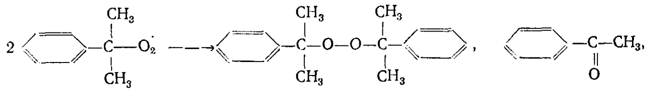
In the oxidation of cumene the chain propagation reaction



$$\mathrm{C_6H_5C(CH_3)_2H}+\dot{\mathrm{O}}_2\mathrm{C(CH_3)_2C_6H_5}\longrightarrow\mathrm{C_6H_5C(CH_3)_2{-}O{-}OH}+\mathrm{C_6H_5\dot{C}(CH_3)_2}$$

leads to the formation of a single primary product—isopropylphenyl hydroperoxide.

The recombination of radicals results in the formation of other oxygen-containing products (dicumenyl peroxide, acetophenone, methylphenylmethanol, etc.):



$$2\,\mathrm{C_6H_5C(CH_3)_2{-}O_2^{\cdot}}\longrightarrow\mathrm{C_6H_5C(CH_3)_2{-}O{-}O{-}C(CH_3)_2C_6H_5},\quad\mathrm{C_6H_5{-}C(=O){-}CH_3},$$

O_2 etc.

In the low-temperature initiated oxidation of hydrocarbons the initiator serves as the source of free radicals in the system and the hydroperoxide does not undergo further transformations. For low degrees of conversion of the hydrocarbon and the initiator, the chain length is almost constant and can be altered by varying the rate of initiation. Under the conditions considered, Eqns.(14) and (15) are transformed as follows:

$$\left.\begin{aligned}S_{\mathrm{ROOH}}&=\frac{\nu}{\nu+m}=\frac{\nu_-^{(\mathrm{O_2})}}{\nu_-^{(\mathrm{O_2})}+1.5}\to 1\\ S_{\mathrm{P_{term}}}&=\frac{1}{\nu+m}=\frac{1}{\nu_-^{(\mathrm{O_2})}+1.5}\to 0\end{aligned}\right\}\ (\text{when } \nu_-^{(\mathrm{O_2})}\gg 1.5).$$

If the rate of reaction is followed from the absorption of oxygen $[\nu=\nu_-^{(\mathrm{O_2})}]$, the coefficient m proves to be 1.5, since two O_2 molecules are absorbed in the chain initiation stage for each free radical formed and evolution of one half of an O_2 molecule corresponds to each $RO_2^{\cdot}$ recombination step.

Fig. 8 presents the dependence of the selectivity in the low-temperature sensitised oxidation of isopropylbenzene on chain length. Evidently, in conformity with the above analysis, for long chains $[\nu_-^{(\mathrm{O_2})}>10]$, the selectivity in the formation of the hydroperoxide is almost independent of ν. For short chains $[\nu_-^{(\mathrm{O_2})}<10]$, a dependence of this kind does appear. The reaction selectivity with respect to chain termination products changes much more, whatever the chain length ν, than the selectivity with respect to the hydroperoxide.

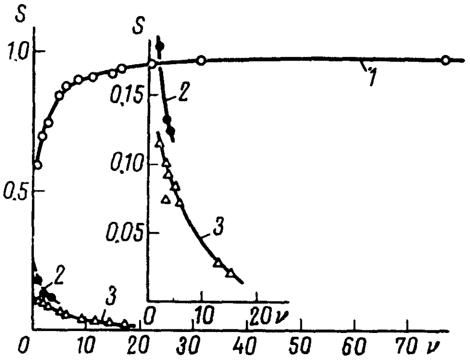
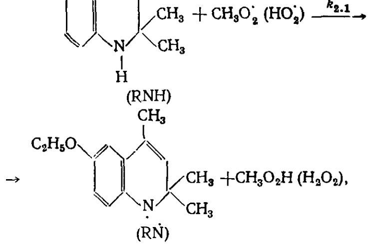


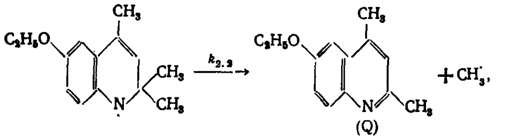
Figure 8. The yields of hydroperoxide (curve *1*), dicumenyl peroxide (curve *2*), and acetophenone (curve *3*) in relation to the amount of absorbed oxygen (in mole %) for different chain lengths in the initiated oxidation of isopropylbenzene. Initiator—azobisisobutyronitrile; solvent—chlorobenzene; temperature 60°C.

The chain oxidation of 6-ethoxy-2,2,4-trimethylethyl-1,2-dihydroquinoline (ethoxyquin, RNH) in chlorobenzene at a temperature >100°C is distinguished by a high selectivity in the formation of 6-ethoxy-2,4-dimethylquinoline (Q).[8] The chain propagation and termination can be represented by the following reactions:

(2.1)



(2.2)



(2.3) $$CH_3^\cdot + O_2 \xrightarrow{k_{2.3}} CH_3O_2^\cdot ,$$

(4) $$RN^\cdot + RN^\cdot \xrightarrow{k_4} \text{products.}$$

The unit of the ethoxyquin oxidation chain consists of a sequence of reactions (2.1), (2.2), and (2.3).

The high selectivity in the oxidation of ethoxyquin to the quinoline at high temperatures is due to the fact that in this process ethoxyquin reacts solely via the reactive N–H bond and the free radical RN$^\cdot$ decomposes via only one pathway (α = 1). Quinoline does not undergo further transformations and is the final reaction product: $\beta = w_-^{(Q)}/w_+^{(Q)} = 0$. The reaction chain length is high ($\nu \geqslant 50$ units) and the selectivity in the oxidation of ethoxyquin to quinoline is more than 95–97 mole % (Fig. 9). The radical RN$^\cdot$ decomposes [reaction (2.2)] with a high activation energy (~20 000 cal mole^{-1}), so that at low temperatures (<50°C) there is virtually no chain oxidation of ethoxyquin. At low temperatures ethoxyquin is used as an effective antioxidant. The high inhibiting activity of ethoxyquin is due to the high rate of reaction (2.1), which takes place with participation of peroxy-radicals ($RO_2^\cdot + RNH \rightarrow RO_2H + RN^\cdot$) and with virtual absence of the decomposition of the RN$^\cdot$ radical.

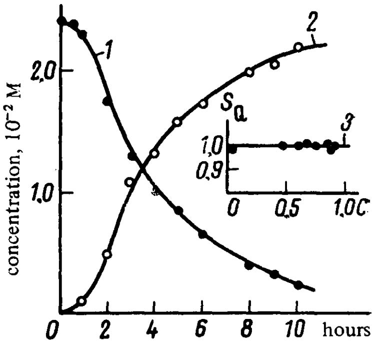


Figure 9. Kinetic curves for the consumption of 6-ethoxy-2,2,4-trimethyl-1,2-dihydroquinoline in the oxidation process (curve *1*) and for the accumulation of 6-ethoxy-2,4-dimethylquinoline (curve *2*); curve *3* represents the selectivity in the formation of quinoline for different degrees of conversion of ethoxyquin. Solvent—chlorobenzene; temperature—120°C.

2. The Influence of Thermal Molecular Decomposition and Chain Consumption of Hydroperoxides on the Selectivity of the Hydroperoxide Oxidation of Hydrocarbons

A high selectivity in the formation of hydroperoxides from aromatic alkyl-substituted hydrocarbons (ethylbenzene, isopropylbenzene, etc.) may obtain at elevated temperatures under conditions where the process occurs in the absence of initiating additives. Active centres are formed in this case when the hydrocarbon reacts with oxygen (chain initiation) and in the decomposition of intermediates (degenerate branching).

Fig. 10 presents kinetic curves for the accumulation of α-phenylethyl hydroperoxides and the consumption of ethylbenzene {Δ[RH]} during its autoxidation[9]. The selectivity in the oxidation of ethylbenzene to the hydroperoxide and its variation with the degree of conversion of the hydrocarbon were calculated from these data (Fig. 10, curve *3*). When the degree of conversion reaches 0.2, the selectivity in the formation of the hydroperoxide falls to 0.82. This decrease cannot be explained solely by the increased rate of initiation in the system, as in the example discussed above [see Fig. 7, Eqn. (16)], since the parameter $k_2[RH]_0/(k_0k_4)^{1/2} = 36M^{1/2}$ in ethylbenzene under the given conditions. According to the calculated data presented in Fig. 7, the process selectivity should greatly exceed 0.9 when C = 0.2.

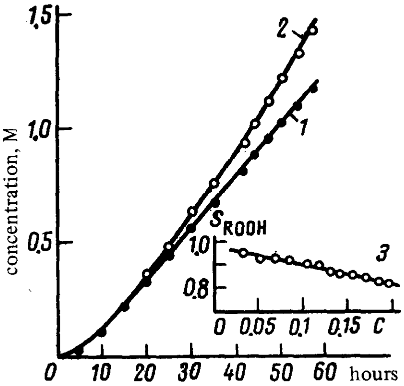


Figure 10. Kinetics of the autoxidation of ethylbenzene at 120°C: 1) the consumption of ethylbenzene Δ[RH]; 2) the accumulation of hydroperoxides; 3) dependence of reaction selectivity with respect to the hydroperoxide $S = [ROOH]/\Delta[RH]$ on the degree of conversion of the hydrocarbon $\Delta[RH]/[RH]_0$. The amount of unconsumed hydrocarbon was calculated from the total amount of products.

The decrease of selectivity during the reaction is caused by the increase of the rates of secondary transformations of the hydroperoxide, which as a rule involves thermal and chain decompositions:

$$RO_2^\cdot + ROOH \xrightarrow{k_2^{01}} R^{\cdot\prime} + \text{alcohol, ketone (chain decomposition),}$$

$$R^{\cdot\prime} + RH \xrightarrow[(+O_2)]{} R'H + RO_2^\cdot .$$

Taking this reaction into account and also the thermal decomposition of the hydroperoxide, the oxidation of ethylbenzene may be represented as a consecutive chain reaction:

$$RH \xrightarrow{+RO_2} ROOH - \left[\begin{array}{l} \xrightarrow[\text{chain decomposition}]{+RO_2^\cdot} \\ \\ \xrightarrow[\text{molecular decomposition}]{} \end{array} \right\} \text{products.}$$

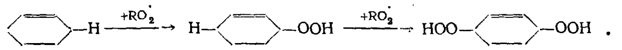
Eqn.(2) for the dependence of process selectivity on the degree of conversion of the initial substance with allowance for chain interaction may be put in the following form:

$$S = \frac{1}{C}\int \frac{\nu(1-\beta)}{(\nu+1+\nu')}\, dC,$$

where $\nu + \nu'$ is the chain length in the consumption of the hydrocarbon and ν is the chain length in the formation of the hydroperoxide. The selectivity with respect to the hydroperoxide must be to a large extent determined by its instability factor:

$$\beta_{ROOH} = \frac{w_-^{(ROOH)}}{w_+^{(ROOH)}} = \frac{k_2^{01}[RO_2^{\cdot}][ROOH] + k_3[ROOH]}{k_2[RO_2^{\cdot}][RH]} = \frac{\nu' + 1/f}{\nu},$$

where $w_-^{(ROOH)}$ is the overall rate of consumption of the hydroperoxide and $w_+^{(ROOH)}$ is the rate of its formation. The quantity β changes during the process (Fig. 10) from 0.06 to 0.4 (for $C = 3-20\%$), which reduces the reaction selectivity with respect to the given product. Paraffins and naphthenes are oxidised at measurable rates at higher temperatures than aromatic alkyl-substituted hydrocarbons. The rate constants for the thermal and chain decomposition of the hydroperoxide are also higher. Under these conditions, β_{ROOH} may be large for lower degrees of conversion of the hydrocarbon, so that the selectivity in the oxidation of paraffins to hydroperoxides is lower than for aromatic alkyl-substituted derivatives. The main cause of the decrease of selectivity in the oxidation of cyclohexene to the monohydroperoxide is its subsequent chain oxidation to the dihydroperoxide, which occurs, like the oxidation of the initial cyclohexene, with participation of the reactive α-C–H bond[10]:



In contrast to the chain consumption of the hydroperoxides of aromatic alkyl-substituted hydrocarbons discussed above, in this elementary stage the OOH functional group of the monohydroperoxide is preserved. Together with the unimolecular decomposition of the hydroperoxide into free radicals and the chain consumption of the hydroperoxide in a secondary chain (with the rate constant k_2^{01}), the oxidation of cyclohexene involves the thermal decomposition of cyclohexenyl hydroperoxide via the reaction

$$RO_2H + HO_2R \overset{K}{\rightleftharpoons} [ROOH \ldots HOOR] \xrightarrow{k_{3.1}} RO^{\cdot} + H_2O + RO_2^{\cdot}.$$

However, the rate of the chain consumption of the hydroperoxide is significantly higher than the rate of its thermal molecular decomposition, so that the cyclohexenyl hydroperoxide "instability factor" may be formulated thus:

$$\beta_{ROOH} = (k_{eff} + k_2^{01}[RO_2^{\cdot}])[ROOH]/\alpha_{(RH\to ROOH)}\, k_2[RO_2^{\cdot}]\cdot[RH] \simeq$$
$$\simeq k_2^{01}[ROOH]/\alpha_{(RH\to ROOH)}\, k_2[RH],$$

where $k_{eff} = k_{3.1}K$ is the effective rate constant for the decomposition of ROOH and $\alpha(RH \to ROOH) = k_{2.1}/(k_{2.1} + k_{2.2})$ is the factor associated with the parallel-reaction mechanism of the main chain in the oxidation of cyclohexene to the monohydroperoxide [$\alpha(RH \to ROOH)$ at 0.7 at 70°C].

Fig. 11*a* presents kinetic curves for the consumption of cyclohexene and the accumulation of cyclohexenyl monohydroperoxide and dihydroperoxide. It is seen from the nature of the kinetic curves that the monohydroperoxide is an intermediate and the dihydroperoxide is a product of the subsequent transformation of the monohydroperoxide. The selectivity in the oxidation of cyclohexene to the monohydroperoxide diminishes from 70 to 20 mole % as the reaction proceeds owing to the increase of the parameter βROOH as C increases from 0 to 60% (Fig. 11*b*).

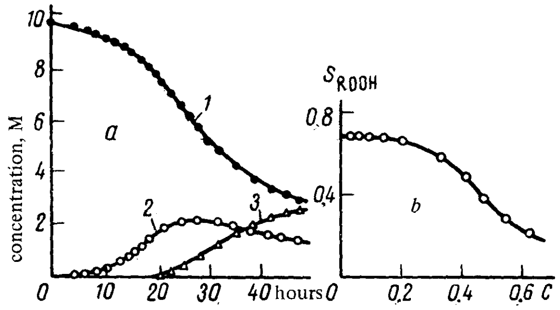


Figure 11. *a*) Kinetic curves for the consumption of cyclohexene (curve *1*) and the accumulation of cyclohexenyl monohydroperoxide (curve *2*) and dihydroperoxide (curve *3*) in the autoxidation of cyclohexene at 70°C; *b*) variation of the selectivity with respect to the monohydroperoxide with increase in the degree of conversion of the hydrocarbon.

3. The Selectivity in a Chain Reaction for the Parallel Consumption of the Hydrocarbon Via Different Pathways

In the general case the hydrocarbon molecule may contain several reaction centres (C–H, C=C, and other bonds), which have different reactivities or their reactivities in relation to reactions with free radicals are similar. The selectivity in the conversion of hydrocarbons into a particular product depends on the ratio of the rate constants for the parallel pathways in the consumption of the hydrocarbon (the quantity α_i). As an example, we may consider the autoxidation of cyclohexene for low degrees of conversion[10]. Cyclohexene is consumed via two parallel pathways with participation of the C–H and C=C bonds and different active centres ($RO_2^{\cdot}$ and $PO_2^{\cdot}$, $RO^{\cdot}$):

$$(2.1)\quad \begin{cases} RO_2^{\cdot} + RH \xrightarrow[(+O_2)]{k_{2.1}} ROOH + RO_2^{\cdot}, \\ PO_2^{\cdot} + RH \xrightarrow[(+O_2)]{k_{2.1}} POOH + RO_2^{\cdot}, \end{cases}$$

$$(2.2)\quad \begin{cases} RO_2^{\cdot} + RH \xrightarrow{k_{2.2}} P^{\cdot}, \\ PO_2^{\cdot} + RH \xrightarrow{k_{2.2}} P^{\cdot}, \end{cases}$$

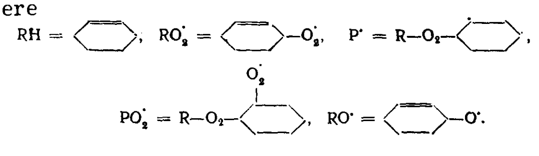
$$(2.3)\quad P^{\cdot} - \begin{cases} \xrightarrow{k_{2.3}} RO^{\cdot} + \text{epoxycyclohexane}, \\ \xrightarrow[(+O_2)]{k'_{2.3}} PO_2^{\cdot}, \end{cases}$$

$$(2.4)\quad RO^{\cdot} + RH \xrightarrow[(+O_2)]{k_{2.4}} ROH + RO_2^{\cdot},$$

$$(2.5)\quad RO^{\cdot} + RH \xrightarrow{k_{2.5}} P^{\cdot},$$

$$\left.\begin{array}{ll} (4.1) & RO_2^{\cdot} + RO_2^{\cdot} \xrightarrow{k_{4.1}} \\ (4.2) & PO_2^{\cdot} + PO_2^{\cdot} \xrightarrow{k_{4.2}} \\ (4.3) & RO_2^{\cdot} + PO_2^{\cdot} \xrightarrow{k_{4.3}} \end{array}\right\}\ \text{products;}$$

where



Analysis of this scheme on the assumption that $k_{2.1}/(k_{2.1} + k_{2.2}) = k_{2.4}/(k_{2.4} + k_{2.5})$ and $k_{4.1} = k_{4.2} = k_{4.3} = k_4$ leads to the following expressions for the concentration of free radicals

$$[\mathrm{R\dot{O}_2}] = \frac{\alpha}{[\alpha + \alpha'(1-\alpha)]}(w_i/k_4)^{1/2},$$

$$[\mathrm{P\dot{O}_2}] = \frac{(1-\alpha)\alpha'}{[\alpha + \alpha'(1-\alpha)]}(w_i/k_4)^{1/2},$$

$$[\mathrm{RO^{\cdot}}] = \frac{k_p}{k_a}\frac{(1-\alpha')(1-\alpha)}{[\alpha + \alpha'(1-\alpha)]}(w_i/k_4)^{1/2},$$

where $k_p = k_{2.1} + k_{2.2}$ and $k_a = k_{2.4} + k_{2.5}$ are the overall rate constants for the consumption of cyclohexene in the interaction with peroxy- and alkoxy-radicals respectively, $\alpha = k_{2.1}/k_p$ and $1 - \alpha = k_{2.2}/k_p$ are the factors associated with the parallel-reaction mechanism of the consumption of cyclohexene involving the participation of the C–H and C=C bonds respectively and $\alpha' = k'_{2.3}[O_2]/\{k_{2.3} + k'_{2.3}[O_2]\}$ is the factor associated with the parallel-reaction mechanism of the consumption of the radical P' via the pathway leading to the formation of PO_2. As in the case considered above, one of the pathways [reaction (2.1)] involves the formation of cyclohexenyl hydroperoxide and products containing a terminal hydroperoxy-group (ROOH), while the other leads to the formation of products resulting from the "saturation" of the carbon–carbon double bond (polymeric peroxide products, epoxycyclohexane, etc.).

The rates of formation of the sum of products [ROOH] + [POOH] + [ROH]‡ = Δ[C–H] and the sum of products which do not contain double bonds {Δ[C=C]} are given by the expressions

$$\mathrm{d}\Delta[\mathrm{C-H}]/\mathrm{d}t = \alpha\nu w_i,$$
$$\mathrm{d}(\Delta[\mathrm{C=C}])/\mathrm{d}t = (1-\alpha)\nu w_i,$$

where

$$\nu = \{k_p([\mathrm{R\dot{O}_2}] + [\mathrm{P\dot{O}_2}]) + k_a[\mathrm{RO^{\cdot}}]\}[\mathrm{RH}]/w_i = k_p[\mathrm{RH}]/(w_ik_4)^{1/2}[\alpha + \alpha'(1-\alpha)] -$$

is the chain length in the consumption of cyclohexene. For a low degree of conversion, where the degrees of the secondary reactions of the products ROOH and POOH are negligibly small, and subject to the condition that the chain is long ($\nu + 1 \simeq \nu$), we have the following relations according to Eqn.(2):

$$S_{[\mathrm{ROOH}]+[\mathrm{POOH}]+[\mathrm{ROH}]^{*}} = S_{\Delta[\mathrm{C-H}]} = \frac{1}{C}\int_0^C \frac{\mathrm{d}([\mathrm{ROOH}] + [\mathrm{POOH}] + [\mathrm{ROH}])}{\mathrm{d}[\mathrm{RH}]}\mathrm{d}C = \alpha,$$

$$S_{\Delta[\mathrm{C=C}]} = \frac{1}{C}\int_0^C \frac{\mathrm{d}(\Delta[\mathrm{C=C}])}{\mathrm{d}[\mathrm{RH}]}\mathrm{d}C = (1-\alpha).$$

If the rate constants for the parallel reactions involving the consumption of the hydrocarbon are associated with different activation energies, the selectivities vary with temperature. Indeed, when

$$k_{2.1} = k^0_{2.1}\exp(-E_1/RT),\ k_{2.2} = k^0_{2.2}\exp(-E_2/RT) \text{ and } E_1 \neq E_2$$

the selectivities are given by the following relations:

$$S_{\Delta[\mathrm{C-H}]} = 1\Big/\left[1 + \frac{k^0_{2.2}}{k^0_{2.1}}\exp(-\Delta E/RT)\right],$$

$$S_{\Delta[\mathrm{C=C}]} = 1\Big/\left[1 + \frac{k^0_{2.1}}{k^0_{2.2}}\exp(\Delta E/RT)\right],$$

where $k^0_{2.1}$ and $k^0_{2.2}$ are pre-exponential factors and $\Delta E = E_2 - E_1$ is the difference between the activation energies. According to these formulae, when $\Delta E > 0$, the selectivity of the reaction via pathway (2.1) decrease with increase of temperature and the selectivity of that via pathway (2.2) increases. This case obtains in the oxidation of cyclohexene. The rate constants for the elementary chain propagation reactions are

$$k_{2.1} = 2.7 \cdot 10^5\exp(-7000/RT) \text{ litre mole}^{-1}\,\mathrm{s}^{-1},$$
$$k_{2.2} = 1.44 \cdot 10^9\exp(-14\,000/RT) \text{ litre mole}^{-1}\,\mathrm{s}^{-1}.$$

Fig. 12*a* presents data for the selectivity in the oxidation of cyclohexene corresponding to degrees of conversion not exceeding 20 mole %, where the rates of the molecular and chain consumption of hydroperoxides are low, i.e. $\beta_{\mathrm{ROOH}} \simeq 0$.[10] It is seen that $S_{\mathrm{ROOH}} = 0.7$ (70%) and $S_{\Delta[\mathrm{C=C}]} = 0.3$ (30%) at 70°C and $S_{\mathrm{ROOH}} = S_{\Delta[\mathrm{C=C}]} = 0.5$ (50%) at 100°C. Fig. 12*b* presents the variation of the selectivity over a wide temperature range. In conformity with the formulae quoted above, the selectivity in the oxidation of cyclohexene to hydroperoxides diminishes and that for the oxidation to products formed as a result of the addition of peroxy-radicals to the C=C bond increases.

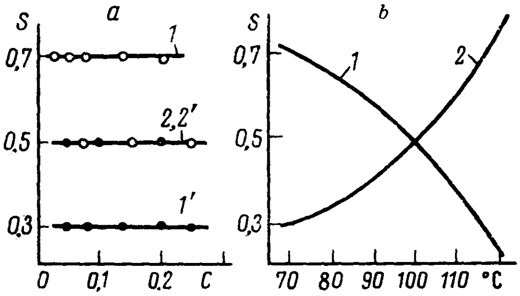


Figure 12. *a*) Dependence of the selectivity in the autoxidation of cyclohexene to the hydroperoxide (S_{ROOH}) (lines *1* and *2*) and to products formed as a result of the oxidation of the C=C bond ($S_{\Delta[\mathrm{C=C}]}$) (lines *1'* and *2'*) on the degree of conversion of the hydrocarbon $C = \Delta[\mathrm{RH}]/[\mathrm{RH}]_0$ at 70°C (lines *1* and *1'*) and 100°C (lines *2* and *2'*); *b*) temperature variation of the selectivities S_{ROOH} (curve *1*) and $S_{\Delta[\mathrm{C=C}]}$ (curve *2*) (calculated data).

4. Selective Inhibition of Undesirable Chain Pathways

In chain reactions proceeding via several active centres with different activities and reactivities, there is a possibility of several parallel pathways some of which lead to the desired product:

$$\mathrm{r^{\cdot}} + \mathrm{A} - \left[\begin{array}{l} \rightarrow \pi \xrightarrow{\mathrm{r^{\cdot}}} \mathrm{P} \text{ (desired product),} \\ \rightarrow \mathrm{M^{\cdot}} \xrightarrow{\mathrm{A}} \mathrm{P_1} \text{ (side product).} \end{array}\right.$$

This also happens when the reactant exhibits a dual reactivity and can be consumed via several pathways under the reaction conditions.

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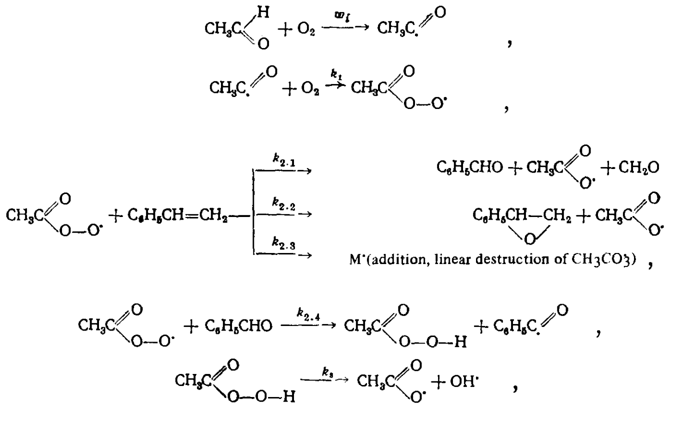
‡ Account is taken of the alcohol formed solely as a result of reactions (2.3) and (2.4).

The conditions governing the possibility of the selective inhibition of the undesirable chain pathway are a difference between the activities of the radicals r· and M· and the absence of their interconversion (the radicals belong to different chains which do not interact). This case obtains in the joint oxidation of styrene and acetaldehyde[11]:

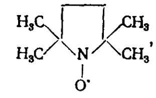


$$\left.\begin{array}{l} M^{\cdot} + O_2 \xrightarrow{k_1'} MO_2^{\cdot} \\ MO_2^{\cdot} + C_6H_5CH{=}CH_2 \xrightarrow{k_2'} M^{\cdot} \end{array}\right\} \text{polymerisation pathway,}$$

etc.

$$MO_2^{\cdot} + MO_2^{\cdot} \xrightarrow{k_{4.1}} P_{term} \ .$$

Stable iminoxy-radicals Im·, in particular tanol



which react with alkyl radicals (M· and $CH_3\dot{C}=O$) at much higher rates than with peroxy-radical $\left(MO_2^{\cdot} \text{ and } RC\begin{smallmatrix}{\diagup\!\!\!\diagup O}\\ {\diagdown O-O^{\cdot}}\end{smallmatrix}\right)$ may be used as the inhibitors of the undesirable polymerisation pathway in this process. Additional chain termination reactions then occur in the system:

$$R\dot{C}{=}O + Im^{\cdot} \xrightarrow{k_{4.2}} P'_{term} \ ,$$

$$M^{\cdot} + Im^{\cdot} \xrightarrow{k_{4.3}} P''_{term} \ .$$

Selective inhibition of the polymerisation pathway is possible when the following condition is fulfilled:

$$w_1 > w_{4.2} \text{ and } w_1' < w_{4.3} \ . \tag{17}$$

Ultimately this implies that the rate of linear termination by the $RO_2^{\cdot}$ radicals must exceed the rate of the interaction of $R\dot{C}{=}O$ with Im·, while the rate of recombination of $MO_2^{\cdot}$ must be much lower than the rate of destruction of M· radicals by the inhibitor:

$$w_{2.3} > w_{4.2} \text{ and } w_{4.1} < w_{4.3} \ . \tag{18}$$

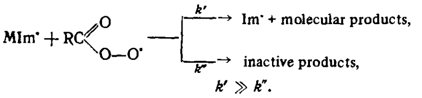
Conditions (17) and (18) hold at an inhibitor concentration

$$\frac{(k_{2.1} + k_{2.2})\,[C_6H_5C_2H_3]}{k_{4.3}} > [Im^{\cdot}] > \frac{(w_0 k_{4.1})^{1/2}}{k_{4.3}} \ . \tag{19}$$

As a rule, condition (19) is fulfilled at very low concentrations [Im·] and requires the artificial maintenance of a steady-state inhibitor concentration in the system during the process.

The inhibition of the polymerisation pathway by the addition of tanol may be achieved by maintaining a steady-state concentration [Im·] as a result of the regeneration of the inhibitor via the mechanism

$$M + Im^{\cdot} \rightarrow MIm^{\cdot},$$



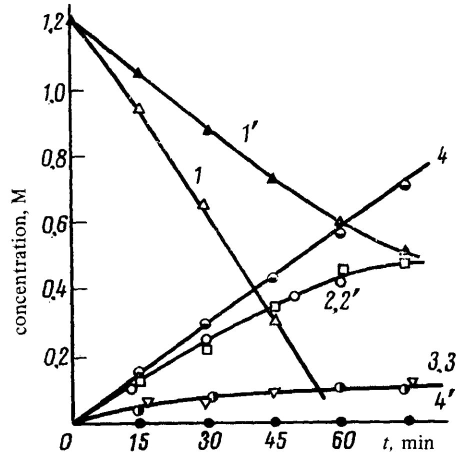


Figure 13. Kinetic curves for the consumption of styrene (curve *1*) and the accumulation of benzaldehyde (curve *2*), 1-phenyloxiran (styrene oxide) (curve *3*), and the polymer (curve *4*) in the joint oxidation of styrene and acetaldehyde in benzene at 70°C; the primed numerals have the same significance but in the presence of 0.002 M of tanol. The instant when the induction period ends was adopted as the time $t = 0$.

Table 1.

Reaction	Required product	Degree of conversion, mole %	Selectivity w.r.t. unsaturated compound which has reacted, mole %	
			without inhibitor	in the presence of Im
Coupled oxidation of styrene and acetaldehyde	1-Phenyloxiran	80.0	40.0	80.0
Coupled oxidation of aryl chloride and acetaldehyde	Chloromethyloxiran	6.0	7.0	65.0
Liquid-phase oxidation of methylacroleine	Methacrylic acid	50.0	30.0	80.0

Fig. 13 presents kinetic curves for the consumption of styrene and the accumulation of its conversion products in the joint oxidation of styrene and acetaldehyde without an inhibitor and in the absence of the iminoxy-radical. Evidently the inhibition of the consumption of styrene is associated with the suppression of its polymerisation (curves *1* and *1'*). To facilitate the comparison, the instant when the consumption of the initial substances begins is adopted as the time $t = t_0$ in both cases. Selective inhibition makes it possible to increase greatly the selectivities of many oxidation processes (Table 1).

5. Homogeneous Catalysis in Oxidation Reactions

Activation of oxygen. One of the possible ways of increasing the rates and selectivities of chemical processes involves the use of homogeneous catalysts—variable-valence metal compounds. This has been established by the activation of O_2, $RO_2^{\cdot}$, or ROOH when they are incorporated in the coordination sphere of the metal. The formation of complexes with all these species has been recorded by various physical procedures. The formation of a complex of O_2 with vitamin B_{12} [a cobalt(II) complex], which involves the generation of the Co(III).$O_2^{\overline{\cdot}}$ species, has been established by ultraviolet spectroscopy (Fig.14*a*),[12] the formation of complexes of Co(II)L_2 with ROOH has been demonstrated by NMR (Fig.14*b*),[13,14] and the formation of complexes of Ni^+ with $RO_2^{\cdot}$ has been demonstrated by ESR (Fig. 14*c*).[15]

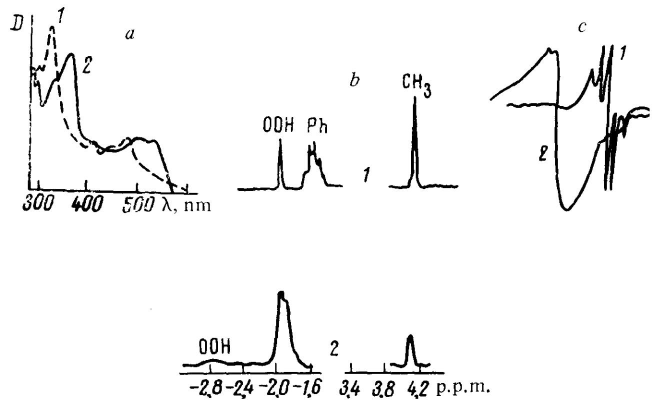


Figure 14. *a*) The spectra of vitamin B_{12} [Co(II)] in methanol at −80°C in an anaerobic medium (curve *1*) and of the B_{12}–oxygen complex formed at p_{O_2} = 1 atm (curve *2*); *b*) the NMR spectra of cumenyl hydroperoxide (c = 0.45 M) in the 1 : 1 CCl_4–CH_2Cl_2 mixed solvent in the absence of a catalyst (curve *1*) and after the addition of 0.0245 M bis-(*o*-vanillideneanisidine)cobalt(II) (curve *2*) at −20°C; *c*) EPR signals due to the nickel(I) species formed in the $Ni(acac)_2 + Al(C_2H_5)_3$ system (curve *1*) and the complex $(CH_3)_3$–C–OȮ.Ni(I) (curve *2*). Solvent—benzene; temperature—23°C.

The use of metal salts rarely leads to an appreciable increase of process selectivity when catalysts of this kind form complexes with virtually all active species and oxygen-containing reaction products (particularly with hydroperoxides and alcohols), since under these conditions the reactions of all the intermediates are accelerated non-selectively. For this reason, the use of metal-complex catalysis is most promising for increasing the selectivity. In this case the use of appropriate ligands or electron-donating additives makes it possible to alter the structure and properties of the catalyst in such a way that the incorporation of one of the reacting species in the coordination sphere becomes unfavourable, and, conversely, the degree of coordination of other substances to the catalyst is enhanced.

Electron-donating ligands greatly increase the ability of cobalt compounds to form adducts with oxygen. The formation of such adducts may be observed by EPR (Fig. 15).[16] The equilibrium constant K_{O_2} for the formation of the complex $Co^{\delta+}L_2(B).O_2^{\delta-}$ via the reaction

$$CoL_2(B) + O_2 \overset{K_{O_2}}{\rightleftharpoons} Co^{\delta+}L_2(B) \cdot O_2^{\delta-}$$

increases with increase of the basicity constant of the base B. Fig. 1 illustrates the dependence of K_{O_2} on the basicity constant of B (pK_B) for the *NN'*-ethylenebis-(benzoylacetoneiminato)cobalt(II) complexes with various electron-donating additives. The inclusion of electron-donating molecules of B in the coordination sphere of cobalt simultaneously lowers the oxidation potential of the complex. There is a correlation between K_{O_2} and the polarographic half-wave potential of the complex. The greater the basicity of B, the lower the value of $E_{1/2}$, i.e. the higher the capacity of the complex $CoL_2(B)$ for being oxidised and hence the higher the degree of electron transfer in $Co^{\delta+}L_2(B).O_2^{\delta-}$, which must increase the activity of the oxygen complex in the formation of free radicals:

$$Co^{\delta+}L_2(B)\,O_2^{\delta-} + RH \rightarrow CoL_2(B)^{\cdot} + HO_2^{\cdot} + R^{\cdot} \quad .$$

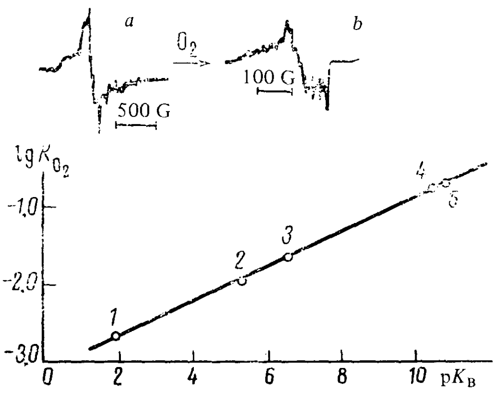


Figure 15. Dependence of the equilibrium constant K_{O_2} for the formation of the O_2 complexes of the adducts of *NN'*-ethylenebis(benzoylacetoneiminato)cobalt(II) with different bases B [1) cyanopyridine; 2) pyridine; 3) 3,4-lutidine; 4) isobutylamine; 5) n-butylamine] on the basicity constants of the latter. The EPR spectra of the adducts *NN'*-ethylenebis(benzoylacetoneiminato)cobalt(II) with pyridine Co(II)L_2Py (*a*) and the complex Co(II)L_2Py.O_2 (*b*).

The decomposition of hydroperoxides by complexes incorporating electron-donating molecules may be retarded owing to steric hindrance to the formation of complexes with the hydroperoxide. There is accordingly an increase of selectivity in the oxidation of hydrocarbons to hydroperoxides. Thus ethylbenzene is oxidised to the hydroperoxide in the presence of cobalt naphthenate with a selectivity $S \simeq 5$ mole % for a degree of conversion $C \simeq 6$ mole %.[17] The introduction of a chelating ligand with pronounced electron-donating properties (quinolinecarboxylic acid) into the solution increase S to 18.9 mole % for C = 8.2 mole % (Table 2).[17]

Nickel compounds, which exhibit a low activity in the decomposition of hydroperoxides but are capable of greatly activating oxygen, make it possible to carry out the oxidation of ethylbenzene with an appreciable selectivity for comparatively high degrees of conversion (Table 2). The selectivity in the oxidation of cyclododecane to ROOH in the presence of bis(acetylacetonato)nickel reaches 46.8 mole % for a degree of conversion of 26.1 mole %.[18] When ethylbenzene is oxidised in the presence of the same catalyst, the selectivity S_{ROOH} = 70 mole% for C_{RH} = 10 mole %. The introduction into the system of small amounts of electron-donating ligands (such as dimethylformamide and NaSt) retards the decomposition of the hydroperoxide and leads to a corresponding appreciable increase of process selectivity (Fig. 16).[19]

Table 2. Selectivity in the oxidation of hydrocarbons to hydroperoxides.

Catalyst	Hydrocarbon	C, mole %	S_{ROOH}, mole %
Cobalt naphthenate	Ethylbenzene	5.9	5.0
Chelate complex of cobalt naphthenate and quinolinecarboxylic acid (B)	Ethylbenzene	8.2	18.9
Bis(acetylacetonato)nickel	Ethylbenzene	10.0	70.0
Bis(acetylacetonato)nickel	Cyclododecane	26.1	46.8

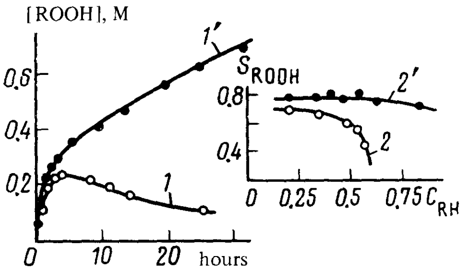


Figure 16. Kinetic curves for the accumulation of hydroperoxides (curves *1* and *1′*) and the dependence of the selectivity in the formation of the hydroperoxide S_{ROOH} on the degree of conversion of the hydrocarbon (curves *2* and *2′*) in the oxidation of ethylbenzene in the presence of 0.003 M Ni(acac)$_2$ (curves *1* and *2*) and a mixture of 0.003 M Ni(acac)$_2$ and 0.003 M dimethylformamide (curves *1′* and *2′*) at 120°C.

The selectivity in the formation of hydroperoxide decomposition products. The composition of the products formed in the decomposition of hydroperoxides in the presence of a catalyst depends on the nature of the solvent[20,21]. The decomposition in the ROOH–catalyst system proceeds via two pathways: with formation of free radicals and molecular products. Both pathways proceed via the formation of a single intermediate complex in accordance with the mechanism[22]

$$\mathrm{Co\,(acac)_2 + ROOH \rightarrow Co\,(acac)_2\,ROOH} \rightarrow$$

$$\rightarrow \underset{\text{(cage)}}{[\mathrm{Co\,(acac)_2^+,\ OH^-,\ RO^{\cdot}}]} \begin{cases} \xrightarrow{k'} \mathrm{Co\,(acac)_2\,OH + RO^{\cdot}} \\ \xrightarrow[k'']{} \mathrm{Co\,(acac)_2 + R'COR'' + H_2O} \end{cases} ,$$

The rate constant ratio k''/k' which determines the fraction of molecular decomposition, depends on the rate of diffusion of RO$^{\cdot}$ from the solvent cage, and increases with increase of the viscosity of the medium (Fig. 17). The ratio of the rate constants for the molecular and radical decompositions of hydroperoxides, which lead in many instances to the formation of different products, depends on the nature of the catalyst, the hydroperoxide, and the solvent[22] (Table 3).

Table 3.

Catalyst	Hydroperoxide	Solvent	$\frac{W_p}{W_\Sigma}\times$ ×100%	Catalyst	Hydroperoxide	Solvent	$\frac{W_p}{W_\Sigma}\times$ ×100%
CoSt$_2$	Tetralinyl	Chlorobenzene	1.2	Ni(acac)$_2$	Tetralinyl	Chlorobenzene	2.0
CoSt$_2$	Cumenyl	Chlorobenzene	36.4	Ni(acac)$_2$	α-phenylethyl	Benzene	4.1
CoSt$_2$	t-Butyl	Benzene	100.0	NiSt$_2$	α-phenylethyl	Ethylbenzene	1.2
Co(acac)$_2$	Cumenyl	Benzene	96.0				

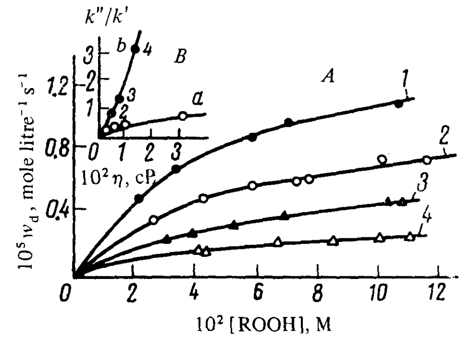


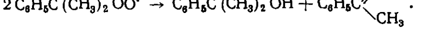
Figure 17. *A*) Dependence of the rate of decomposition of cumenyl hydroperoxide in the presence of 5 × 10^{-4} M Co(acac)$_2$ on [ROOH] in benzene (curve 1) and in solvents with mobile C–H bonds [2) ethylbenzene; 3) a mixture of 60 vol.% of tetralin and benzene; 4) tetralin]; *B*) dependence of k''/k' on η for the decomposition of cumenyl hydroperoxide in inert solvents (*a*) and in solvents with mobile C–H bonds (*b*). Points *2*, *3*, and *4* were obtained from the data represented by curves 2, 3, and 4 in Fig. *A*.

Cumenyl hydroperoxide decomposes in the presence of CoSt$_2$ via a chain mechanism with formation of dimethylphenylmethanol and acetophenone:

$$\mathrm{C_6H_5C\,(CH_3)_2\,OOH + CoSt_2 \rightarrow C_6H_5C\,(CH_3)_2\,CO^{\cdot} + Co(OH)St_2},$$

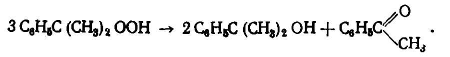
$$\mathrm{C_6H_5C\,(CH_3)_2\,OOH + Co\,(OH)\,St_2 \rightarrow C_6H_5C\,(CH_3)_2\,OO^{\cdot} + CoSt_2 + H_2O},$$

$$\mathrm{C_6H_5C\,(CH_3)_2\,OOH + C_6H_5C\,(CH_3)_2\,O^{\cdot} \rightarrow C_6H_5C\,(CH_3)_2\,OH + C_6H_5C\,(CH_3)_2\,OO^{\cdot}},$$



$$\mathrm{2\,C_6H_5C\,(CH_3)_2\,OO^{\cdot} \rightarrow C_6H_5C\,(CH_3)_2\,OH + C_6H_5C(=O)CH_3}\ .$$

The stoichiometric equation for the process is



$$3\,C_6H_5C(CH_3)_2OOH \rightarrow 2\,C_6H_5C(CH_3)_2OH + C_6H_5C(=O)CH_3 .$$

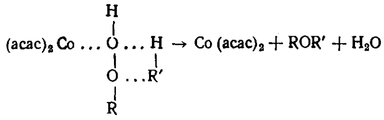
As expected on the basis of the mechanism, the process selectivity with respect to dimethylphenylmethanol $S_{C_6H_5C(CH_3)_2OH} \simeq 70$ mole %.

The selectivity in the chain decomposition of the hydroperoxide may be increased by adding hydrogen donors which react readily with peroxy-radicals and lead to a change in the chain termination mechanism. For example, the introduction of an inhibitor leads to the replacement of the $RO_2^{\cdot}$ (the source of the ketone) recombination reaction by the reaction

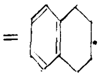
$$C_6H_5C(CH_3)_2OO^{\cdot} + InH \rightarrow C_6H_5C(CH_3)_2OOH + In^{\cdot}.$$

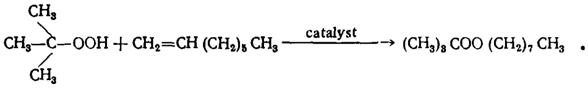
The experimental process selectivity then increases to 95 mole %.[4]

The activation of the hydroperoxide in the catalyst sphere makes it possible to achieve many bimolecular reactions of ROOH with hydrocarbons. In the decomposition of cumenyl hydroperoxide in the presence of hydrocarbons with a mobile C–H bond, there is an appreciable increase in the contribution of molecular decomposition of the hydroperoxide, although the overall rate of decomposition remains constant. The ether ROR′ is then formed in the system as a result of the reaction between the hydrocarbon and the activated hydroperoxide via the mechanism[23]



$$(acac)_2Co \ldots O(H)(OR) \ldots H(R') \rightarrow Co(acac)_2 + ROR' + H_2O$$

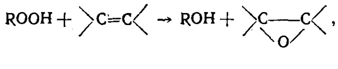
where ROOH = $C_6H_5C(CH_3)_2OOH$ and R′H = . When ROOH interacts with the hydrocarbon R′H, there is a possibility of the formation of the asymmetric peroxides ROOR′:



$$CH_3-C(CH_3)_2-OOH + CH_2{=}CH(CH_2)_5CH_3 \xrightarrow{\text{catalyst}} (CH_3)_3COO(CH_2)_7CH_3 .$$

In the decomposition of t-butyl hydroperoxide in cyclohexene, oct-1-ene, or cumene in the presence of copper, manganese or cobalt salts the selectivity in the formation of asymmetric peroxides reached 90 mole %.[25]

Molybdenum, vanadium, and tungsten compounds are known to catalyse the bimolecular reaction[26,27]



which constitutes the basis of the highly selective synthesis of olefin oxides (the "chalcone process"). It has been shown recently that this reaction proceeds via the intermediate formation of a complex of ROOH with the catalyst. The formation of such complexes is indicated by the broadening of the absorption band of the hydroperoxide protons in the NMR spectrum of t-butyl hydroperoxide under the influence of dioxobis(cyclohexanediolato)molybdenum[28,29] and bis(acetylacetonato)molybdenyl[30].

The change in the hydroperoxide decomposition pathway and the increased selectivity of this process are the most important factors, which make it possible to increase the selectivity in oxidation reactions.

The change in the chain reaction pathway. The high selectivities (above 95 mole %) in the oxidation of aromatic alkyl-substituted hydrocarbons to organic acids may be achieved by employing cobalt bromide in acetic acid as the catalyst. Manganese(II) compounds are used as promoting additives, which lead to an additional increase of reaction selectivity. The mechanism of catalysis by cobalt compounds in the presence of bromide ions still remains controversial.

Although the specific mechanism of the formation of acids is not clear, it may be that the oxidation proceeds via a radical-chain mechanism where the catalyst is involved in the chain propagation reaction according to the following mechanism:

Formation of cobalt bromide:

$$CoAc_2 + NaBr \rightleftharpoons CoAcBr\,(Co\,(II)\,Br^-) + NaAc.$$

Chain initiation:

$$ROOH + Co\,(II) \rightarrow RO^{\cdot} + Co\,(III) \xrightarrow{RH} ROH + R^{\cdot} + Co\,(III),$$

$$ROOH + Co\,(III) \rightarrow RO_2^{\cdot} + Co\,(II).$$

Chain propagation:

$$R^{\cdot} + O_2 \rightarrow RO_2^{\cdot},$$

$$RO_2^{\cdot} + RH \rightarrow ROOH + R^{\cdot},$$

$$RO_2^{\cdot} + Co\,(II) \xrightarrow{HAc} ROOH + Co\,(III),$$

$$RO_2^{\cdot} + Co\,(II)\,BrH^+ \rightarrow ROOH + Co\,(III)\,Br^- \rightarrow ROOH + Co\,(II)\,Br^{\cdot}.$$

Bromide chain propagation:

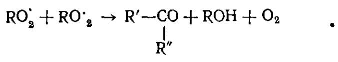
$$Co\,(III)\,Ac_3 + Co\,(II)\,Br^- \rightarrow Co\,(II)\,Ac_2 + Co\,(III)\,Br^-Ac \rightarrow Co\,(II)\,Br^{\cdot}Ac$$

$$Co\,(II)\,Br^{\cdot}Ac + RH \rightarrow Co\,(II)\,Ac_2 + HBr + R^{\cdot} \rightarrow Co\,(II)\,\dot{B}r^-Ac + HAc + R^{\cdot}.$$

Overall reaction:

$$Co\,(III)\,Ac_3 + RH \rightarrow Co\,(II)\,Ac_2 + HAc + R^{\cdot} .$$

Chain termination:



$$RO_2^{\cdot} + RO_2^{\cdot} \rightarrow R'-CO(R'') + ROH + O_2 .$$

In the presence of the cobalt bromide catalyst, the chain oxidation pathway, consisting in alternate reactions of the $R^{\cdot}$ radicals with O_2 and of $RO_2^{\cdot}$ radicals with the hydrocarbon, is replaced by a new more complex chain pathway which leads to a higher process selectivity.

This apparently occurs as a result of the suppression of the undesirable pathways involving the formation of peroxy-radicals and the hydroperoxide.

6. Simulation of Enzymatic Processes

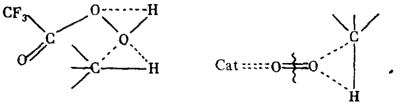
In the development of selective oxidation processes it is frequently proposed to use the principles of the simulation of enzymatic oxidation which in many cases involve a high selectivity with respect to the substrate oxidised. A characteristic feature of the mechanism of an enzymatic process is activation of the reactants, coupling of the reactions, and a highly organised matrix [templet] nature of the process.

Hydroxylation. In biological systems this process takes place under the influence of mono-oxygenases as a coupled reaction involving the oxidation of the substrate and on organic reductant AH_2 present in the system[31]:

$$AH_2 + RH + O_2 \rightarrow A + ROH + H_2O .$$

The ratios of the amounts of the alcohol formed, the unconsumed organic reductant, and the oxygen absorbed are 1 : 1 : 1. The selectivity in the oxidation reaction with respect to the substrate reaches 100 mole % for low degrees of conversion.

It is suggested that the enzymatic oxidation of hydrocarbons proceeds via the oxenoid mechanism [32] in a concerted process in which an oxygen atom of the O_2 molecule, activated by the enzyme, is inserted in a C–H bond of the substrate without the formation of free radicals. In chemical systems the oxenoid mechanism can occur when acyl hydroperoxides react with RH and in the catalytic epoxidation of olefins by hydroperoxides:



Depending on the nature of the enzyme and the substrate, the oxidation proceeds via different mechanisms. In the hydroxylation of 2,6-di-t-butyl-4-methylphenol, catalysed by an enzymatic system containing cytochrome P-450, the accumulation of the hydroperoxide was observed at early stages of the oxidation process. It appears that in this instance oxygen is inserted, without the association of the O–O bond, via the mechanism [33]

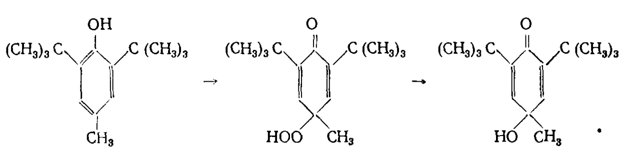
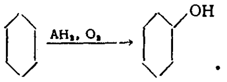


Table 4. Coupled oxidation of cyclohexane (S_1 and S_2 are respectively the selectivities in the formation of the alcohol and the ketone in terms of consumed cyclohexane and S_3 is the selectivity in the formation of the alcohol in terms of the consumed reductant).

System	S_1, mole%	S_2, mole %	S_3, mole %	System	S_1, mole %	S_2, mole %	S_3, mole %
Mono-oxidase	100	—	100	$SnCl_2$	100	—	5
Fe^{2+} + ascorbic acid	75	25	4	$TiCl_2$	95	5	8
Haemin + thiosalicylic acid	60	40	8	$FeCl_2$	80	20	9

In recent years numerous attempts were made to simulate enzymatic oxidation processes. The condition which must be met by such simulation is believed to be the simultaneous transfer of two electrons to the O_2 molecule [34]. Such electron transfer is possible in the oxidation of a metal capable of transferring two or more electrons [for example, $SnHPO_4$, $SnCl_2$, $MoCl_3$, and $Mo(CO)_6$ in Table 4] or of a ligand in a system of the Fe^{2+}–ascorbic acid type. However, in the known model systems there is at present no direct evidence for the occurrence of the oxenoid hydroxylation mechanism, characteristic of enzymatic systems, i.e. O is inserted in a C–H bond in a single step. On the other hand, model systems make it possible to hydroxylate alkanes with a high selectivity (Table 4) under mild conditions. In such systems the process apparently proceeds via a coupled radical chain mechanism.

The principle of the coupled oxidation of hydrocarbons and tin compounds has been used for the selective oxidation of hydrocarbons to alcohols (hydroxylation):



The selectivity in the formation of alcohols with respect to the hydrocarbon is close to 100 mole %. [34,35] This result has been obtained in the coupled oxidation of cyclohexane and $SnCl_2$ in acetonitrile at 20°C with formation of cyclohexanol as the only cyclohexane conversion product. The kinetic mechanisms for the oxidation of cyclohexane in the absence of $SnCl_2$ and after the introduction of bivalent tin into the reaction are compared below:

"Classical" oxidation mechanism	Coupled oxidation of RH and tin
(0) $RH \rightarrow R^{\cdot}$	(0) $\begin{cases} Sn(II) + O_2 \rightarrow Sn(III) + HO_2^{\cdot} \\ HO_2^{\cdot} + RH \rightarrow H_2O_2 + R^{\cdot} \end{cases}$
(1) $R^{\cdot} + O_2 \rightarrow RO_2^{\cdot}$	(1′) $R^{\cdot} + O_2 \rightarrow RO_2^{\cdot}$
(2) $RO_2^{\cdot} + RH \rightarrow ROOH + R^{\cdot}$	(2′) $RO_2^{\cdot} + Sn(III) + H_2O \rightarrow ROH + Sn(IV)OH^-$
(3) $ROOH \rightarrow RO^{\cdot}$	(3′) $ROOH + Sn(II) \rightarrow RO^{\cdot} + Sn(III)OH^-$
(4) $RO^{\cdot} + RH \rightarrow ROH + R^{\cdot}$	(4′) $RO^{\cdot} + Sn(III) + H_2O \rightarrow ROH + Sn(IV)OH^-$
(5) $ROOH \rightarrow$ ketone	(5′) $ROOH + Sn(II) + H_2O \rightarrow Sn(IV)(HO^-)_2 + ROH$
(6) $RO_2^{\cdot} + RO_2^{\cdot} \rightarrow$ molecular products	(6′) $Sn(III) + Sn(III) \rightarrow Sn(II) + Sn(IV)$

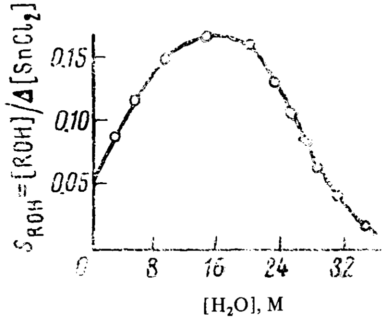


Figure 18. Dependence of the selectivity in the formation of cyclohexanol with respect to unconsumed $SnCl_2$ on the concentration of water in the coupled oxidation of cyclohexane and $SnCl_2$ at 20°C.

The high process selectivity is due to the replacement of the chain propagation reaction (2) involving the hydrocarbon by reaction (2′) involving Sn(III) in the reaction chain and is also due to a change in the hydroperoxide decomposition pathway. In the presence of tin(II) the hydroperoxide decomposes via a molecular pathway with formation of an alcohol [reaction (5)]. The selectivity of this process with respect to the reductant ($SnCl_2$) is low (up to 5 mole %), which may imply a considerable consumption of the reductant in processes which are useless from the standpoint of the formation of the desired product (the alcohol). The selectivity in the utilisation of the reductant may be somewhat increased by altering the composition of the medium. Thus, when the reaction is carried out in a mixed solvent (acetonitrile–water), the reaction selectivity with respect to the reductant increases to 20 mole % (Fig. 18).

Epoxidation of olefins. The coupled oxidation reactions may become a promising method for increasing the selectivity of processes of this type. In order to obtain the required product, active centres propagating a parallel chain process involving the conversion of the second component of the coupled pair are employed.

Catalytic systems for the direct oxidation of propene to epoxypropane are being actively sought at the present time. A yield of epoxypropane not less than 75 mole % relative to the unconsumed propene is believed to be economically useful. In the absence of a catalyst in glass, Teflon, or titanium reactors the selectivity in the direct oxidation of propene to epoxypropane does not exceed 50 mole % relative to the unconsumed propene (even for a low degree of conversion—up to 10–20 mole %).[36]

Fig. 19 presents kinetic curves for the oxidation of propene in chlorobenzene at 150°C and 50 atm. When propene is oxidised under these conditions, more than 20 products are formed, 14 of which are listed in Fig. 19; others are formed as impurities. In view of such complex mixture compositions, the isolation of the individual products presents significant technical difficulties.

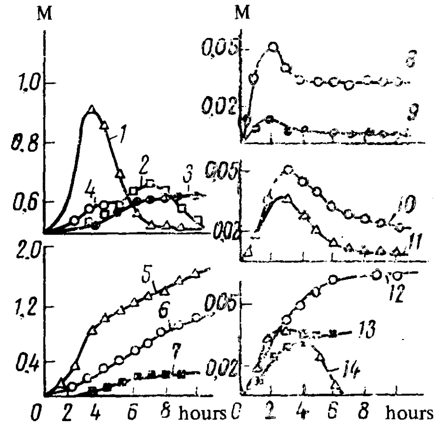
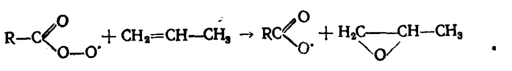


Figure 19. Kinetic curves for the accumulation of propene oxidation products: 1) epoxypropane; 2) propylene glycol; 3) propylene glycol formate; 4) CO_2; 5) formic acid; 6) acetic acid; 7) methyl formate; 8) acetaldehyde; 9) peroxide; 10) isopropyl alcohol; 11) allyl alcohol; 12) acetone; 13) methanol; 14) acrolein.

In the coupled oxidation of propene and acetaldehyde the epoxidation of the double bond proceeds with participation of acylperoxy-radicals formed as a result of the oxidation of the aldehyde[37]:



This reaction has a close analogy with enzymatic oxidation processes, since an oxygen atom is inserted (in a single elementary step) in the molecule of the substance undergoing oxidation with dissociation of the O–O bond. The coupled process proceeds at comparatively low temperatures (50–70°C) and is distinguished by high selectivities in the formation of acetic acid from acetaldehyde (~100%) and of epoxypropane from propene (~100%) (Fig. 20).

The main disadvantage of systems simulating enzymatic oxidation is the consumption of the reductant together with the main process. In many instances the selectivity relative to the unconsumed reductant proves to be very low. Consequently the main task involved in increasing the selectivity of the oxidation reaction is not so much the simulation of enzymatic processes as the creation of new effective catalytic systems which are in general highly effective and do not require the consumption of the second component (the reductant).

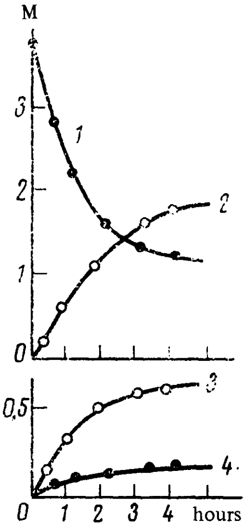


Figure 20. Kinetic curves for the consumption of acetaldehyde (curve 1) and the accumulation of acetic acid (curve 2) epoxypropane (curve 3), and propylene (curve 4) in the coupled oxidation of propene and acetaldehyde at 50 atm and 70°C.

All the enzymatic and model reactions discussed above involve the dissociation of the O–O bond. Catalytic processes in which oxygen adds via a hydrocarbon (olefin) activation stage are apparently more effective. Here oxygen is transferred to the substrate from water or adds on directly. The oxidation of olefins to carbonyl compounds catalysed by palladium(II) salts using $CuCl_2$ as a cocatalyst is an example of reactions of this type. The selectivity in the formation of low-molecular-weight aldehydes in such a process is >95 mole %.[38] The process develops via the mechanism

$$PdCl_4^{2-} + C_2H_4 + H_2O \rightarrow Pd^0 + CH_3CHO + 2H^+ + 4Cl^- ,$$

$$Pd^0 + 2Cu^{2+} + 8Cl^- \rightarrow PdCl_4^{2-} + CuCl_2^- ,$$

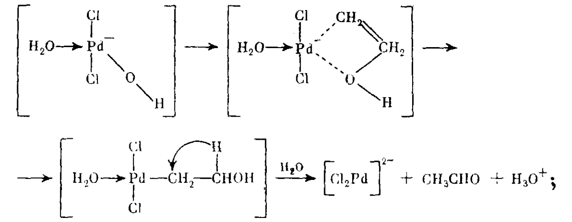
$$2\,CuCl_2^- + 1/2O_2 + 2H^+ \rightarrow 2Cu^{2+} + H_2O + 4Cl^- .$$

The overall reaction is

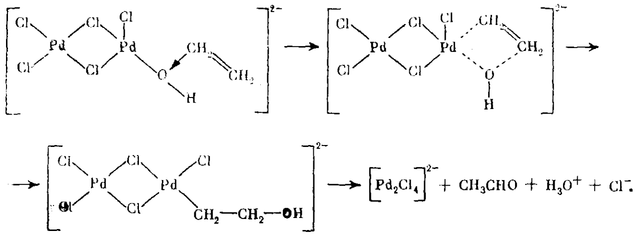
$$C_2H_4 + 1/2O_2 \rightarrow CH_3CHO + 52.26 \text{ kcal mole}^{-1}.$$

A significant factor is the formation in the system of π-complexes $(C_2H_4)PdCl_2(OH^-)$, which undergo further transformations via two possible pathways:

pathway I:



pathway II:



Studies where heteropolyacids of complex composition and containing molybdenum and vanadium ions are used instead of $CuCl_2$ have developed[39]. This makes it possible to eliminate Cl^- ions from the process. The oxidation then proceeds with a high selectivity because of the absence of parallel chlorination reactions in which a considerable proportion of the unreacted hydrocarbon is consumed in the oxidation of higher olefins.

Alcohols and ketones are selectively oxidised to acids in alkaline media in the presence of copper complexes of *o*-phenanthroline (*o*-phen). The oxidation of methanol in the presence of $Cu(o\text{-phen})_2^{2+}$ in alkaline media leads to the formation of formaldehyde and acetic acid at very high rates even at 25–30°C.[40,41] Under the same conditions, certain aliphatic ketones (ethyl methyl ketone) are selectively oxidised to acids[42]. The process develops via the intermediate formation of a complex of the carbanion $CH_3C(O)\bar{C}HCH_3$ (A^-) with $Cu(o\text{-phen})_2^{2+}$:

$$[Cu(o\text{-phen})_2\,A^-]^+ \rightleftharpoons [Cu(o\text{-phen})_2A^\cdot]^+,$$

$$[Cu(o\text{-phen})_2A^\cdot]^+ + O_2 \rightarrow [Cu(o\text{-phen})AO_2^\cdot]^+,$$

$$[Cu(o\text{-phen})_2AO_2^\cdot]^+ + [Cu(o\text{-phen})_2]^{2+} + OH^- \rightarrow 2[Cu(o\text{-phen})_2]^+ + 2CH_3COOH.$$

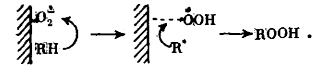
The last two cases may be regarded as examples of oxidation processes which are more favourable from the standpoint of their selectivity than even enzymatic processes.

7. Heterogeneous Catalysis in Oxidation Reactions

The liquid-phase oxidation of hydrocarbons in the presence of heterogeneous catalysts proceeds via two different mechanisms.

I. A heterogeneous-homogeneous process with formation of radicals on the surface of the catalyst and their subsequent transfer to the liquid phase[43-45]. The catalyst merely initiates the chain reaction, the process selectivity remaining the same as in the absence of the catalyst and only the rate of reaction being altered. The liquid-phase oxidation of ethylbenzene in the presence of Ag_2O may serve as an example[46]. The reaction proceeds via a chain mechanism with short chains and the formation of methylphenylmethanol and acetophenone in the chain termination steps. These catalysts are active in the decomposition of the hydroperoxide and the selectivity in the formation of ROOH is as a rule low.

II. A heterogeneous process without the liberation of radicals to the bulk phase[47] may proceed via the mechanism



The formation of the $O_2^{\dot{-}}$ species has been demonstrated in gas-phase oxidation in the presence of deposited catalysts and in the liquid-phase oxidation of cumene (Fig. 21).[48,49] The possibility, in principle, of obtaining high yields of peroxides then arises, since such catalysts do not as a rule decompose ROOH and free radicals are not formed in the bulk phase (the hydroperoxide does not decompose via a chain mechanism).

The conditions under which the $RO_2^\cdot$ radicals are not released into the bulk phase and hydrocarbons are oxidised on the catalyst surface as a result of the activation of oxygen are achieved by employing the method of the donor–acceptor modification of the catalyst[49]. The catalyst is modified by the introduction of additives to the gas, liquid, and solid phases. This entails a change in both the rate of the process and in its selectivity. When the Ag_2O catalyst is used, electron-accepting properties are shown by oxygen, the hydroperoxide, alcohol, 2,4,6-dicyanomethylenetrinitrofluorenone, etc. The activity of the modified catalysts in relation to the decomposition of the hydroperoxide is highly suppressed and the process selectivity with respect to the hydroperoxide is significantly increased.

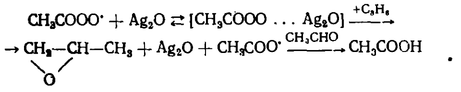
Table 5. Selective catalytic systems for the oxidation of aromatic alkyl-substituted hydrocarbons to hydroperoxides.

Catalyst	Additive	S_{ROOH}, mole %	S_{ROH}, mole %	$S_{RC(O)R}$, mole %	C, mole %
	Oxidation of ethylbenzene				
Ag_2O	—	20.0	50.0	30.0	1.3
Ag_2O	Cumenyl hydroperoxide (Na salt)	81.0	11.0	8.0	0.5
Ag/Al_2O_3	—	20.0	50.0	30.0	2.5
Ag/Al_2O_3	Acetophenone + methylphenylmethanol	77.0	19.2	3.8	1.8
Ag/Al_2O_3	0.2 at.% Ca	54.5	19.5	26.0	0.6
Ag/Al_2O_3	0.2 at.% Ca + acetophenone + methylphenylmethanol	96.0	3.0	1.0	0.6
	Oxidation of tetralin				
Ag_2O	—	10.0	26.0	64.0	6.0
Ag/SiO_2	—	18.0	36.0	46.0	7.5
Ag/SiO_2	Tetralinol + tetralinone	93.0	2.2	1.8	6.3

Modification also occurs under the influence of the reaction products (Table 5). In this case the process selectivity increases with increased degree of conversion. Thus in the oxidation of tetralin the reaction is non-selective at early stages—the hydroperoxide, ketone, and alcohol accumulate in equal amounts[50]. With increase in the degree of conversion of tetralin, the decomposition of the hydroperoxide ceases and only oxygen is activated on the catalyst modified by the oxidation products, as a result of which tetralinyl hydroperoxide becomes the only reaction product (Table 5).

In order to increase the selectivity of the oxidation process, deposited catalysts are modified. The modification of the Ag/Al_2O_3 deposited catalyst by the addition of calcium makes it possible to increase the selectivity in the oxidation of ethylbenzene to the hydroperoxide from 20 to 54.5 mole %, while modification by the 0.2 at.% Ca–acetophenone–methylphenylmethanol system increases the selectivity S_{ROOH} to 96 mole %.[50]

Heterogeneous catalysis in coupled oxidation[51]. An important parameter of the synthesis of epoxypropane and acetic acid is the "coefficient of the utilisation of active oxygen", i.e. the selectivity in the formation of epoxypropane with respect to the aldehyde which has reacted (γ). In the absence of a catalyst (at 70°C in benzene under a pressure of 50 atm) $\gamma = 0.3$. The use of silver oxide as the heterogeneous catalyst makes it possible to increase γ considerably (Table 6). In this case the process proceeds with participation of complexes formed by peroxy-radicals with the catalyst:



$$CH_3COOO^{\cdot} + Ag_2O \rightleftarrows [CH_3\dot{C}OOO \ldots Ag_2O] \xrightarrow{+C_3H_6}$$
$$\rightarrow \underbrace{CH_2-CH}_{O}-CH_3 + Ag_2O + CH_3COO^{\cdot} \xrightarrow{CH_3CHO} CH_3COOH \quad .$$

Table 6. Coupled oxidation of propene and acetaldehyde at 70°C and 50 atm (solvent—benzene).

System	Selectivity, mole %		
	w.r.t. C_3H_6	w.r.t. CH_3CHO	w.r.t.CH_3CHO
	Epoxypropane		Acetic acid
Without catalyst	95.0	23.0	92.0
Ag_2O (1.0 g $litre^{-1}$)	98.0	63.0	96.0

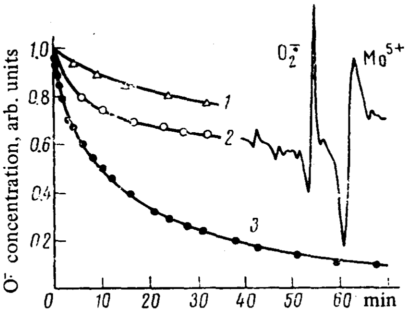
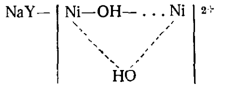


Figure 21. The EPR spectrum of the O_2^- radical-anion detected in the liquid phase on the surface of the Mo(V)/MgO heterogeneous catalyst and kinetic curves for its consumption in various hydrocarbons at 20°C:
1) ethylbenzene; 2) cumene; 3) cyclohexene.

Catalysis of oxidation on zeolites. Nickel-zeolite is a highly effective catalyst of the gas-phase oxidation of methanol by oxygen (350°C).[52] The process selectivity depends on the conditions in the preparation of the catalyst, particularly on the pH of the medium. In acid media the nickel on the zeolite exists in the form of isolated ions ($NaY\ldots Ni^{2+}$). The process on the catalyst then proceeds with formation of dimethyl ether as the main reaction product (acid–base mechanism).

When media close to neutrality (at pH from 7 to 7.6) are used, the nickel on the zeolite exists in the form of the complex



$$NaY-\left|\begin{matrix} Ni-OH-\ldots Ni \\ \diagdown\quad\diagup \\ HO \end{matrix}\right|^{2+} \quad .$$

This complex exhibits a high magnetic susceptibility and an oxidation-reduction process proceeds on the catalyst. The presence of the OH group in the catalytic complex facilitates the electron transfer and the formation of formaldehyde and other oxidation products (Fig. 22). Thus, by altering the magnetic susceptibility of the catalyst, it is possible to influence the selectivity of oxidation processes.

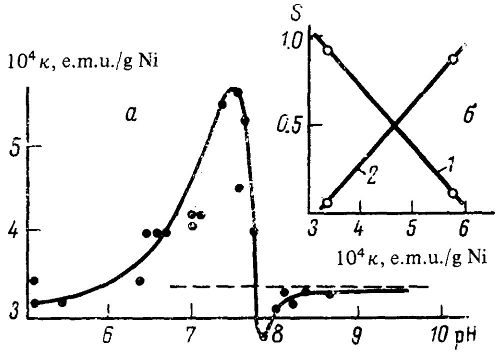


Figure 22. *a*) Dependence of the magnetic susceptibility of nickel (κ) in zeolites on the pH in the ion-exchange process; the dashed line represents the magnetic susceptibility of nickel ions; *b*) selectivity in the conversion of methanol: 1) into dimethyl ether CH_3OCH_3; 2) into oxidation products (CO_2, CO, and formaldehyde) as a function of the magnetic susceptibility of nickel-zeolite.

VII. RADICAL POLYMERISATION PROCESSES

The concept of selectivity applied to polymerisation processes may be considered in two ways: (1) the formation of a definite molecular structure for homopolymers or a definite tacticity, regularity, branching, and inhomogeneity of composition for copolymers; (2) the formation of a product with a specified molecular weight distribution (MWD) and specified average molecular weights (the distribution moments M_{N}).

The classical mechanism of radical polymerisation includes the following stages:

1. Initiation

$$R_0^{\cdot} + M \rightarrow M_1^{\cdot} \quad .$$

2. Chain propagation:

$$M_n^{\cdot} + M \rightarrow M_{n+1}^{\cdot} \quad ,$$
$$M_n^{\cdot} + X \rightarrow P_n + R_1^{\cdot} \quad \text{(chain transfer).}$$

3. Chain termination:

$$\dot{M}_n + \dot{M}_m \rightarrow P_{n+m} \quad \text{(recombination)},$$
$$\dot{M}_n + \dot{M}_m \rightarrow P_n + P_m \quad \text{(disproportionation)}.$$

The narrowest MWD for the polymer is obtained under isothermal conditions of synthesis and the width of the distribution is determined by the mechanism of the termination of the growing chains. Termination owing to the recombination of radicals leads to the so-called Schultz distribution ($\bar{M}_W/\bar{M}_N = 1.5$), while termination via the disproportionation of radicals leads to the normal distribution ($\bar{M}_W/\bar{M}_N = 2.0$). The reaction involving chain transfer to the monomer, solvent, initiator, etc. leads to an exponential distribution.

The width of MWD in radical polymerisation may be increased by various procedures which may be of practical importance in the industrial synthesis of products with the required physicochemical and rheological properties, provided that the "optimum" properties of the material occur in the region of broad MWD. It appears that this happens in the case of the main thermoplastics synthesised on a large scale: high- and low-density polyethylene, poly(vinyl chloride), and polystyrene. In order to improve the rheological properties of melts of these materials, the MWD must be fairly broad ($\bar{M}_W/\bar{M}_N \geqslant 2.0$).

1. Regulation of the Rates of Chain Termination in Radical Polymerisation

The classical concept of the mechanism of radical polymerisation as a typical chain reaction in which the chain length is regulated by the rate of chain termination makes it possible to control the polymerisation process by altering the rate of chain initiation[53]. It is also possible to control the elementary stages of the process by the interaction of the monomer and the chain propagation radical with the reaction medium.

The reactivities of monomers and radicals change as a result of their combination with the molecules of the medium. Certain modifying agents may alter the conjugation energy and the distribution of electron densities in the monomer and the radical. If the modifying agents participate in the formation of a transition complex, they naturally influence its energy, configuration, and chemical nature. This changes the free-radical chain propagation mechanism to a complex-radical mechanism. However, the influence of the medium cannot be reduced solely to chemical aspects of the interaction.

Regulation of the rates of chain termination. The use of the gel-effect. The influence of initiating additives. The elementary reaction involving the bimolecular destruction of macroradicals at early stages of homogeneous liquid-phase polymerisation is controlled by physical factors and depends on the physical characteristics of the reaction medium and the macromolecules formed.

The Norrish–Trommsdorff effect (gel-effect—acceleration of radical polymerisation after the accumulation in the system of a sufficient amount of the dissolved polymer) is an example of the dominant influence of physical factors on the kinetics of homogeneous polymerisation processes. The manifestation of the gel-effect is attributed to the aggregation of macromolecules and the formation in the polymerising system of a continuous three-dimensional fluctuation network, in which the macro-radicals are "stuck"[54,55]. This retards the destruction of the active centres via recombination or disproportionation. On the other hand, the active centres are accessible to the monomer molecules and the growth of the polymer chain continues for some time. For high degrees of conversion, the chain propagation reaction passes to the diffusion-dependent region.

The nature of the diffusion-dependent limitations imposed on the elementary reactions in radical polymerisation is determined by the physical characteristics of the macromolecules and the macroradicals and also by the intermolecular interactions in the system. Using the effects associated with the interaction of the monomers and radicals with the reaction medium, it is possible to control the elementary stages of radical polymerisation by means of both chemical and physical factors.

By creating a highly viscous system, by using low monomer concentrations, or by introducing additives which ensure high rates of chain initiation, it is possible to alter the rate of the biradical chain termination. An increase of the concentration of the initiator in the polymerising mixture makes it possible to maintain a specified MWD up to high degrees of conversion of the initial monomer. Such a system may approach "live" (without termination) polymerisation.

2. Polymerisation in the Devitrification of Reaction Mixtures (Supercooled Liquid)

Radical-chain polymerisation processes hardly occur when the system is in the vitreous state owing to the low mobility of the species and the low temperature despite the high concentration of active centres. However, these reactions proceed very effectively when the system passes from the vitreous to the supercooled liquid state. The fairly high viscosity of the supercooled liquid prevents the bimolecular destruction of the active centres and the reaction develops via a "live" chain mechanism (Table 7). The interaction of the reacting centre with the matrix of the monomer (for example, methyl acrylate) plays an important role in the selectivity of such reactions[56,57]. In the devitrification of the alcohol matrix the macroradical has a specific conformation which ensures its long life. As a result, intense polymerisation takes place in the system.

Table 7. Chain propagation rate constants (cm^3 s^{-1}).

Polymerisation	$10^{12}\cdot k_p^0$	E, cal mole^{-1}	$10^3\cdot k_p^0$	E, cal mole^{-1}	$10^{18}\cdot k_p^0$	E, cal mole^{-1}
	Crystal		Devitrification		Liquid	
Acrylic acid	6	11 000	5	10 700	20	3000
Methyl acrylate	—	—	1	10 000	2	4700
Methyl methacrylate	—	—	Does not polymerise		0.8	4700

Fig. 23 presents the EPR spectra of free polymer radicals obtained on γ-irradiation of frozen solutions of acrylic acid in ethanol (17%), recorded at different temperatures (with a gradual increase of the temperature of the solution). Spectrum I was obtained at 77 K and represents a superposition of the EPR spectra of the radicals $CH_3\dot{C}HOH$ and $CH_3\dot{C}HCOOH$. The stabilised electron also makes some contribution to the structure of the spectrum. When the specimen is heated to 110 K (supercooled liquid), the radical concentration diminishes (the intensity of the spectrum falls). The EPR spectrum of the radical measured for the same system (spectrum II) consists of five well resolved components with the intensity ratios 1 : 2 : 2 : 2 : 1, which corresponds to the *B* conformation of the radical with the angle $\varphi = 75°$. In this system the interaction between the alkyl group and the COOH(*x*) group is weakened, which is the reason for the long life of the radicals (the formation of "live" radicals). With increase of temperature above 120 K, the polymer chain acquires the capacity for translational migrations. The macroradical coils up and has the usual conformation (*A* in Fig. 23) with the angle $\varphi = 15°$, which corresponds to a triplet EPR spectrum (spectrum III).

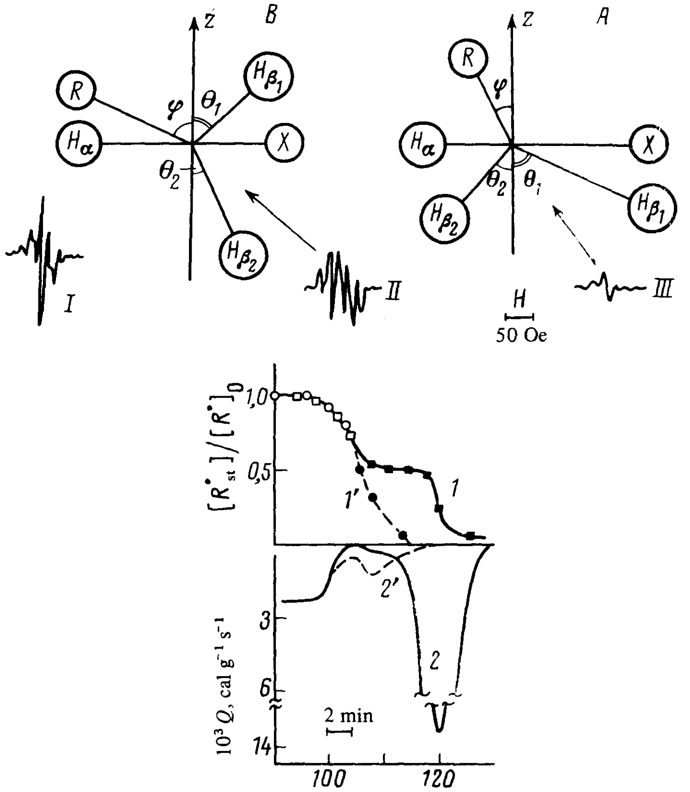


Figure 23. Temperature dependence of the steady-state concentration of radicals (curves *1* and *1'*) and of the rate of polymerisation (calorimetric curves *2* and *2'*) in γ-irradiated frozen solutions of acrylic (curves *1* and *2*) and methacrylic (curves *1'* and *2'*) acids in ethanol: I)–III) EPR spectra arising on heating the γ-irradiated acrylic acid solution in ethanol to 77, 110 (*B* conformation) and 125 K (*A* conformation) respectively.

The polymerisation of acrylic acid at 100–110 K with devitrification of the matrix (i.e. under conditions where "live" radicals are formed in the system) proceeds at very high rates. Curve *2* in Fig. 23 represents the change in the rate of polymerisation measured calorimetrically during the heating of the specimen. After a characteristic "step" associated with the transition to the supercooled liquid state, heat is evolved due to polymerisation. The radical concentration in this temperature range changes only slightly (Fig. 23, curve *1*). In the polymerisation of methacrylic acid the conformation corresponding to "live" radicals is not formed, since the presence of the methyl group prevents the interaction of the radical with the alcohol matrix. The lifetime of the radical is short, the radical concentration decreases monotonically with increase of temperature (Fig. 23, curve *1'*), and the post-polymerisation effect is not observed (Fig. 23, dashed curve *2'*).

In the viscous supercooled liquid formed on devitrification, the duration of mutual contact between the reactants is much longer than in the gas and liquid phases. For this reason, the composition of the copolymer obtained in a viscous supercooled liquid is independent of the relative reactivities of the comonomers and is determined solely by their initial concentrations[58]. The composition of the acrylic acid–acrylamide copolymer does indeed fully correspond to the initial solution on devitrification of the alcohol matrix, while in solution the copolymerisation constants for these monomers are different and the composition of the copolymer differs from that of the initial solution. Thus the method makes it possible to synthesise polymers with a specified homogeneity of composition.

Structure formation by macromolecules. By controlling the macromolecular structure formation processes during the polymerisation, it is possible to exclude fully the reaction involving the destruction of macroradicals and thus pass to an outwardly homogeneous liquid system with radical polymerisation via the "live" chain mechanism[59–63].

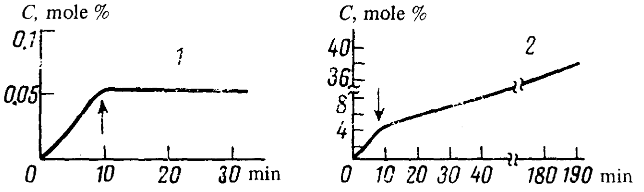


Figure 24. Kinetics of the polymerisation (*C* is the degree of conversion) of methyl methacrylate in bulk (curve *1*) and in a mixture with orthophosphoric acid (curve *2*). The arrow indicates the instant when light was switched off.

It has been shown that in the photoinitiated polymerisation of methyl methacrylate (MMA) in a mixture with orthophosphoric acid the reaction continues, after switch-off the initiation source, at a constant albeit somewhat lower rate up to high degrees of conversion (Fig. 24). The number of chains remains unaltered during post-polymerisation. The reaction proceeds as a result of the accumulation in the "light stage" of poly(methyl methacrylate) (PMMA) macroradicals, which are not involved in the bimolecular termination reaction[59,64,65]. The introduction of another monomer after the exhaustion of the initial methyl methacrylate leads to the renewal of polymerisation and the formation of block-copolymers[66]. The cause of the preservation of the number of growing chains (macroradicals) in these outwardly homogeneous solutions is the formation of a stable fluctuation network with participation of PPMA macroradicals, strengthened by a network of hydrogen bonds between the $COOCH_3$ groups in the PMMA units and H_3PO_4.

Radical post-polymerisation without termination may be achieved also by the slow heating of vitreous monomers or their mixtures with complex-forming agents subjected to preliminary irradiation at −196°C with γ-rays or ultraviolet light. The post-polymerisation of butyl methacrylate in the presence of $ZnCl_2$ may serve as an example of such a process. These processes may be followed by EPR and calorimetric methods[67]. In the transition through the devitrification regions some of the radicals accumulated as a result of irradiation are destroyed, while the remaining radicals continue to grow and further post-polymerisation proceeds virtually via a mechanism without chain termination.

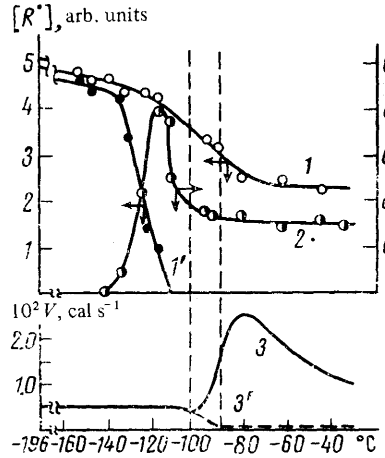


Figure 25. Post-polymerisations in the γ-irradiated butyl methacrylate (BMA)−$ZnCl_2$ system (1 : 0.45). Variation of the concentration of the sum of the radicals (curves *1* and *1'*) and oligomeric $(BMA)_n^{\circ}$ radicals (curve *2*) and of heat evolution (curves *3* and *3'*) in the system on polymerisation in the presence of $ZnCl_2$ (curves *1*–*3*) and in the absence of a complex-forming agent (curves *1'*–*3'*). The dashed lines are the limits of the devitrification region.

The post-polymerisation proceeds with participation of oligomeric radicals. Irradiation of frozen solutions (−196°C) of butyl methacrylate (BMA) leads to the formation of monomeric radicals, the EPR spectrum of which consists of seven lines (ΔH = 22.5 G). On raising the temperature to between −150° and −130°C, a monomer molecule adds to the radical and oligomeric radicals are produced. The concentration of monomeric radicals falls and oligomeric radicals accumulate in the system. At temperatures between −130° and −110°C the system contains only oligomeric radicals (Fig.25).

In the range between −100° and −80°C the main bulk of the radicals recombine, but, in contrast to the polymerisation of BMA in the absence of $ZnCl_2$, a steady-state concentration $[(BMA)_n^{\bullet}]$ is established in the system, which ensures rapid post-polymerisation at this temperature. This results in the formation of polymers with a fairly narrow MWD, whose molecular weights are specified by the irradiation dose and are defined by the formula

$$\overline{M}_n = \frac{q[BMA]}{[R^{\bullet}]},$$

where q is the degree of conversion, [BMA] the monomer concentration, and $[R^{\bullet}]$ the concentration of radicals.

Thus one of the problems involved in increasing the selectivity of polymerisation processes, namely the formation of a product with a specified molecular weight distribution, may be solved by influencing the rate of recombination of macroradicals by changing the reaction temperature, irradiation of the solution, or the introduction of complex-forming agents.

Radiation-induced graft polymerisation. Using the influence of the viscosity of the medium on the rate of bimolecular chain termination, it was possible to develop a new method of radiation-induced graft polymerisation[68]. The usual radiation-induced polymerisation of the monomer is comparatively slow or leads to the formation of a polymer with a low molecular weight. If a small polymer "seed" is subjected to preliminary irradiation and then introduced into the monomer, the degree of conversion increases by a factor of several hundred and a polymer with a high molecular weight is formed. The essential feature of the effect is that the radicals formed in the solid "seed" and propagating the polymerisation chain hardly recombine. As a result, the yield of the polymer and its molecular weight increase by several orders of magnitude.

The method has been applied to the synthesis of Teflon by the polymerisation of tetrafluoroethylene[68]. Irradiation of tetrafluoroethylene with a dose of 0.05 Mrad leads to the formation of Teflon with a low yield and a low molecular weight. The employment of a "seed" increases the yield of Teflon by a factor of 200 and its molecular weight by two orders of magnitude.

3. Polymerisation in Continuous Operation Reactors

An important factor influencing the MWD arises when the reactions are carried out in ideal mixing or plug flow reactors[69,70]. The broadening or narrowing of the MWD when the process passes from the periodic to the continuous-operation regime depends under these conditions on the lifetime of the active centre. A criterion of the broadening of the MWD on passing to the continuous-regime is the inequality $\tau_c \ll \tau$, where τ_c is the average lifetime of the active centres and τ the residence time of the species in the ideal mixing reactor. The method used to carry out the reaction also has a regulating effect on the composition of the polymer in copolymerisation.

Whereas the monomers reacting at different rates in a periodic-operation reactor give rise to a variable-composition copolymer, in an ideal mixing reactor the process proceeds at a constant rate, which results in the formation of a copolymer with a homogeneous composition[71]. In certain cases it is useful to carry out the polymerisation in a cascade of reactors with different process regimes.

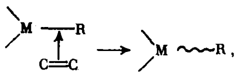
The optimum process conditions are determined in this instance by analysing the kinetic model of the process using mathematical simulation methods.

Such studies have been carried out for the radical polymerisation of styrene in bulk[72]. It was established that the optimum composition of the polymer may be achieved by carrying out the polymerisation in a cascade of reactors consisting of two series-connected ideal mixing reactors, in which the process is carried out in different temperature regimes, and an ideal plug flow reactor with an adiabatic regime.

The MWD of the final product is somewhat narrower compared with the calculated distribution owing to the mechanochemical effects in the extrusion of the melt. This procedure yields a product with $\bar{M}_W/\bar{M}_N = 2.7-3.0$, which is fairly close to the empirically observed "optimum" in the mechanical and rheological properties of a thermoplastic of this type.

4. Homogeneous Catalysis

The molecular weight distribution of the macromolecules may be narrowed by polymerising olefins in the presence of soluble catalysts. In such cases the polymer chain is grown in the coordination sphere of a transition metal:



i.e. the macroradical is linked to the metal throughout the entire polymerisation process. In contrast to purely radical processes, chain termination takes place mainly via unimolecular reactions. The chain-transfer reactions in these processes are inhibited and there is virtually no branching of the macromolecules.

The narrowest molecular weight distributions of polyethylene may be obtained by use of the soluble catalytic systems $(C_2H_5)_2TiCl_2 + AlR_2Cl$, in which the catalytic centres are homogeneous[73,74]. The general polymerisation mechanism can be represented as follows:

$$X^{\cdot} + M \xrightarrow{k_i} M_1^{\cdot},$$
$$M_1^{\cdot} + M \xrightarrow{k_p} M_2^{\cdot},$$
$$M_j^{\cdot} + M \xrightarrow{k_p} M_{j+1}^{\cdot},$$
$$M_j^{\cdot} \xrightarrow{k_t} r_j + X^{\cdot},$$
$$M_j^{\cdot} \xrightarrow{k_d} r_j,$$

where $X^{\cdot}$ and M are the active centre and the monomer and k_i, k_p, k_t, and k_d are the initiation, chain propagation, chain transfer, and chain termination constants. The theoretical form of the molecular weight distribution is defined by the expression

$$L_j = \{M_j + r_j\}_1^{\infty},$$

where M_j and r_j are the concentrations of "live", i.e. growing, and non-growing ("dead") chains. The theoretical MWD may be compared with experimental data using the integral expression[74]

$$\frac{jL_j}{\sum\limits_{j=1}^{\infty} jL_j} \cdot 100 = W_j' = \frac{w_i}{2} + \sum_{\alpha=1}^{j-1} w_{\alpha}.$$

Calculations have shown that the ratio $\bar{M}_W/\bar{M}_N = 1.8-2.2$. The values obtained agree satisfactorily with the experimental ratios $\bar{M}_W/\bar{M}_N$.

Fig. 26 presents the MWD for polyethylene obtained by radical catalytic polymerisation. Evidently the use of a homogeneous catalyst leads to a sharp narrowing of the MWD, i.e. to an increase of the polymerisation selectivity.

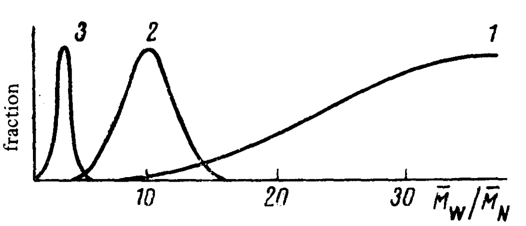


Figure 26. Molecular weight distributions for high-pressure (curve *1*) and medium-pressure (curve *2*) polyethylenes and in catalytic polymerisation in the presence of a homogeneous catalyst (curve *3*).

A narrow molecular weight distribution ($\bar{M}_W/\bar{M}_N \leq 2$) in polypropylene was obtained in a study[75] where propene was polymerised in heptane at low temperatures (between −20° and −60°C) in the presence of the $VCl_4 + AlEt_2Cl$ catalytic system, which exists in a homogeneous state under these conditions. With increase of temperature (above −10°C), the solid catalyst appeared and the MWD was greatly broadened ($\bar{M}_W/\bar{M}_N$ increased to 30).

Catalysis of radical addition. Regulation of the composition of copolymers. Radical copolymerisation is usually regarded as a statistical process in which the probabilities of the addition of monomers to the growing chain are determined by their concentrations and the nature of the substituent at the double bond. In this case copolymerisation proceeds via the mechanism

$$(1.1)\ m_1^{\cdot} + M_1 \xrightarrow{k_{1.1}} \sim m_1m_1^{\cdot}\,(\sim m_1^{\cdot}),$$
$$(1.2)\ m_1^{\cdot} + M_2 \xrightarrow{k_{1.2}} \sim m_1m_2^{\cdot}\,(\sim m_2^{\cdot}),$$
$$(2.1)\ m_2^{\cdot} + M_1 \xrightarrow{k_{2.1}} \sim m_2m_1^{\cdot}\,(\sim m_1^{\cdot}),$$
$$(2.2)\ m_2^{\cdot} + M_2 \xrightarrow{k_{2.2}} \sim m_2m_2^{\cdot}\,(\sim m_2^{\cdot}),$$

where $m_1^{\cdot}$ and $m_2^{\cdot}$ are the terminal units of the growing polymer chain formed by the addition of the molecules M_1 and M_2 respectively; the first subscript in the constants refers to the terminal monomeric unit of the macroradical.

The composition of the copolymer depends on the rate constant ratios $k_{1.1}/k_{1.2} = r_1$ and $k_{2.2}/k_{2.1} = r_2$ and is defined by the formula

$$\frac{d[m_1^{\cdot}]}{d[m_2^{\cdot}]} = \frac{[M_1]}{[M_2]} \cdot \frac{r_1[M_1] + [M_2]}{r_2[M_2] + [M_1]}\ . \tag{20}$$

There exist many binary systems where copolymerisation leads to the formation of copolymers with a rigorous alternation of monomeric units ($m_1m_2m_1m_2$), i.e. the limiting selectivity in the chain propagation reaction is reached. In certain cases this occurs also without the use of any special additives by virtue of the chemical nature of the specific monomer pairs. In particular, α-olefins, certain dienes, and vinyl ethers (M_1) form on radical initiation rigorously alternating copolymers with maleic anhydride, certain other maleic acid derivatives, and SO_2 (M_2).

However, combinations of this kind are more likely to be exceptional. In most instances the reactivities of the monomers do not promote a rigorous alternation of elementary steps of types (1.2) and (2.1) in the mechanism quoted above. In particular, α-olefins, vinyl ethers, and dienes are incapable of forming alternating copolymers with the majority of known monomers. Furthermore, the double bonds in olefins and vinyl ethers are relatively inactive and enter with difficulty into reactions of types (1.2) and (2.1). Their involvement in radical copolymerisation is therefore in general difficult. Finally, an additional obstacle arises in the case of α-olefins—degradative chain transfer to the monomer leading to the formation of relatively inactive radicals of the allyl type and the corresponding sharp decrease of the probabilities of all four chain propagation reactions.

The above complications can be overcome and rigorously alternating copolymers can be obtained from the above monomers of the M_1 group with vinyl monomers of the type $CH_2{=}CHX$, where X = COOR, CN, or C(O)R (acrylates, methacrylates, acrylonitrile, etc.) by carrying out the radical copolymerisation in the presence of complex-forming agents—Lewis acids ($AlRCl_2$, $SnCl_4$, $ZnCl_2$, etc.).

It has been shown by a number of methods, in particular by direct observations with the aid of EPR of the sequence of elementary steps (initiation and chain propagation) leading to the formation of the molecules of alternating copolymers, that the polymerisation is in all cases a radical-chain reaction initiated by monoradicals [64]. Depending on the nature of the monomers and the reaction conditions, chain propagation takes place via the consecutive addition of either individual monomers molecules or of donor–acceptor complexes ($M_1 \ldots M_2$) to the growing chain radical via the mechanism

$$(1.2)\quad \sim \dot{m}_1 + M_2 \xrightarrow{k_{1.2}} \sim m_1\dot{m}_2\,,$$

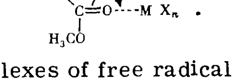
$$(2.1)\quad \sim \dot{m}_2 + M_1 \xrightarrow{k_{2.1}} \sim m_2\dot{m}_1\,,$$

$$(1.2\ \text{c})\quad \sim \dot{m}_1 + (M_2 \ldots M_1) \xrightarrow{k^c_{1.2}} \sim m_1m_2\dot{m}_1\,,$$

$$(2.1\ \text{c})\quad \sim \dot{m}_2 + (M_1 \ldots M_2) \xrightarrow{k^c_{2.1}} \sim m_2m_1\dot{m}_2\,.$$

The copolymerisation of maleic anhydride with 2,3-dimethylbutadiene [67,76] and phenyl vinyl ether [64], of methyl methacrylate with 2,3-dimethylbutadiene in the presence of $Al(C_2H_5)_2Cl$, [67,76,77] etc. are examples of systems where reactions (1.2) and (2.1) predominate. Chain propagation takes place via the addition of donor–acceptor complexes of the comonomers [reaction (1.2c) and 2.1c)] in the copolymerisation of SO_2 with 2,3-dimethylbutadiene or vinyl acetate [76] and of maleic anhydride with butyl vinyl ether [64]. All types of chain propagation reactions coexist simultaneously in many instances (copolymerisation of maleic anhydride with vinyl acetate [64,79]).

The mechanism of copolymerisation in the presence of Lewis acids includes the formation of a complex of the Lewis acid with free polymeric radicals ($\sim \dot{m}_1$ or $\sim \dot{m}_2$) or monomers [80–82]:



The formation of complexes of free radicals with $AlCl_3$, $AlBr_3$, etc. has been demonstrated by EPR on the basis of the systematic changes occurring in the EPR spectra of radicals in the presence of these compounds [80] (Figs. 27*A* and 27*B*).

Quantum-mechanical calculations have shown that donor–acceptor interactions between the radical and the species which adds to it lower the free energy of formation of the transition complex in the reactions

$$\sim \dot{m}_1 + M_2 \rightarrow (\sim m_1 \ldots M_2) \rightleftarrows (\sim m_1^- \ldots M_2^+) \rightarrow \sim m_1\dot{m}_2$$

or

$$\sim m_1 + (M_2 \ldots M_1) \rightarrow (\sim m_1 \ldots \dot{M}_2 \ldots M_1) \rightleftarrows (\sim m_1^- \ldots M_2^+ \ldots M_1) \rightarrow$$
$$\rightarrow \sim m_1m_2\dot{m}_1\ .$$

Table 8. Copolymerisation of butyl methacrylate with 2,3-dimethylbutadiene in the presence of Lewis acids.

Initiator	Temp., °C	$[MX_n]/[M_1]$	r_1	r_2	r_1r_2
		$MX_n = ZnCl_2$			
[ABIBN] = 0.005 M	50	0	0.45±0.01	0.47±0.03	0.212
		0.15	0,23±0.05	0.41±0.10	0.094
		0.25	0.10±0.01	0.40±0 03	0,040
		$MX_n = Al(C_2H_5)_2Cl$			
u.v. (λ > 313 nm)	15	0.10	0.11±0.042	0.048±0.036	0.0053
		0.25	0.058±0 018	0.013±0.015	0.0007
		0.15	0.044±0.027	0.010±0.024	0,004

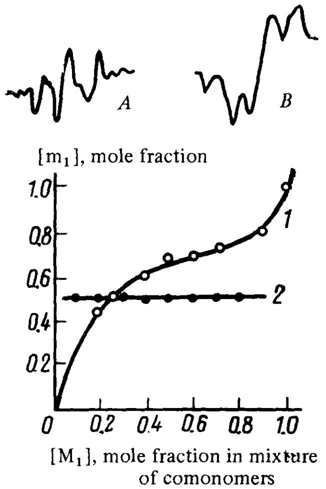


Figure 27. Copolymerisation of butyl methacrylate (M_1) with 2,3-dimethylbutadiene (M_2) at 23°C in the presence of $Al(C_2H_5)_2Cl$ for different $[Al(C_2H_5)_2Cl]/[M_1]$ ratios: 1) 0.10; 2) 0.55; *A* and *B* are the EPR spectra of the polymeric radical $\sim \dot{m}_1$ and the complex $[\sim \dot{m}_1 \ldots AlBr_3]$ for $[AlBr_3]/[M_1] = 1$.

As a result of the increase of the rate constants $k_{1.2}$ and $k_{2.1}$, the quantities r_2 and r_1 (see above) decrease with increased concentration of the complex-forming agent, which in this case actually behaves as the selective catalyst of radical addition (Table 8). For very low values of r_1 and r_2 ($r_1 \rightarrow 0$ and $r_2 \rightarrow 0$), the ratio of the monomeric units m_1 and m_2 in the copolymer is according to Eqn.(20)

$$d[m_1]/d[m_2] = 1 \text{ and } [\overline{m}_1] = [\overline{m}_2]\,,$$

and a fully alternating copolymer is formed regardless of the initial concentrations of the comonomers in solution. Fig. 27 illustrates the dependence of the copolymer composition (the fraction of m_1) on the composition of the mixture of comonomers in the copolymerisation of butyl methacrylate (M_1) with 2,3-dimethylbutadiene (M_2) in the presence of $Al(C_2H_5)_2Cl$.[80] With increase of catalyst concentration, there is an increase in the selectivity of the copolymerisation. For fairly high values of $[Al(C_2H_5)_2Cl]$, it is possible to attain conditions under which a fully alternating polymer is formed $\{[m_1] = [m_2] = 0.5\}$ over a wide range of monomer content M_1 in the mixture (from 5 to 95%). Alternating copolymerisation via reactions (1.2c) and (2.1c) is the limiting case of non-statistical radical processes.

It has been observed[64] in the copolymerisation of SO_2 with buta-2,3-diene that the nature of the terminal unit of the growing radical is specified by the nature (donor–acceptor properties) of the initiating radical and does not change in the course of chain propagation. Depending on the type of initiating radical, the radicals $\sim SO_2^{\cdot}$ and $\sim CH_2-\underset{CH_3}{C}\overset{\cdot}{\dashrightarrow}\underset{CH_3}{C}\overset{\cdot}{\dashrightarrow}CH_3$, which propagate two independent polymerisation chains, can therefore exist in different proportions. In the case under consideration, the introduction of the catalyst enhances the differences between the reactivities of the radicals in relation to the comonomers (r_1, $r_2 \rightarrow 0$ after the addition of the catalyst).

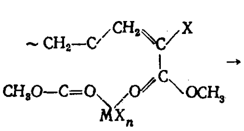
In the copolymerisation of monomers having functional groups of the same type (for example, COOR) in the presence of Lewis acids there is a possibility of another limiting case—the "disappearance" of the differences between the reactivities of the monomers in the chain propagation reaction ($r_1 \rightarrow 1$ and $r_2 \rightarrow 1$). This effect was observed in the copolymerisation of methyl methacrylate with methyl acrylate in the presence of $ZnCl_2$ and $AlBr_3$ [83] and was subsequently confirmed in certain other systems[64].

Table 9. Copolymerisation of methyl methacrylate (M_1) with methyl acrylate (M_2) in the presence of complex-forming agents at 50°C.

Initiator	$\frac{[MX_n]}{[M_1]+[M_2]}$	r_1	r_2
	$MX_n = ZnCl_2$		
[ABIBN] = 0.005 M	0	2.23±0.13	0.36±0.1
	0.15	1.33±0.03	0,70±0.03
	0.45	0.90±0.03	0,90±0,09
	$MX_n = AlBr_3$		
u.v. (λ > 313 nm)	0.075	1.75±0.04	0.78±0.05
	0.15	1,11±0.04	0,91±0.1
	0.40	0,96±0,05	0.96±0.11

Table 9 lists the effective constants for the copolymerisation of methyl methacrylate (M_1) with methyl acrylate (M_2) in the presence of $ZnCl_2$ and $AlBr_3$.[83] When the catalyst MX_n is added, the composition of the copolymer, initially relatively enriched in M_1 units, approaches that of the mixtures of the monomers and becomes virtually identical with it when $[MX_n]/\{[M_1] + [M_2]\} = 0.2-0.5$; under these conditions, the effective copolymerisation constants are $r_1 = r_2 = 1$ (Fig. 28).

The equalisation of the relative activities of the comonomers following the introduction of complex-forming agents can be naturally accounted for within the framework of the hypothesis that chain propagation proceeds via a stage involving a cyclic transition complex with simultaneous coordination of the radical and the monomer to the MX_n molecule:



→ chain propagation.

The mutual approach and appropriate orientation of the reaction centres of the monomer and the radical promote rapid addition. The probability of addition virtually ceases to depend on the true reactivities of the radical and the monomer. The mechanism of chain propagation in radical homo- and co-polymerisation in systems of this kind is in principle analogous to the typical mechanisms of coordination-ionic polymerisation. The stability of the complex of the modifying agent and the terminal unit of the growing radical increases owing to the delocalisation of the unpaired electron of the radical to the metal ion in MX_n.[80] The resulting possibility of the migration of MX_n with retention of the complex at the terminal unit of the growing chain increases the analogy with coordination-ionic polymerisation still further.

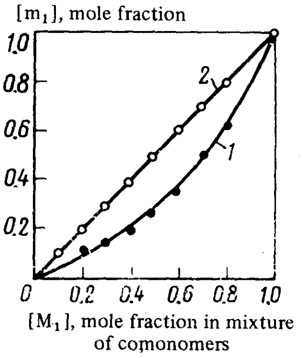


Figure 28. Copolymerisation of methyl methacrylate (M_1) with methyl methacrylate (M_2): 1) in the absence of complex-forming agent; 2) after the introduction of zinc chloride; $[ZnCl_2]/\{[M_1] + [M_2]\} = 0.25$; temperature 50°C.

5. The Influence of Magnetic and Electric Fields

An urgent problem in polymer chemistry is the synthesis of stereoregular and crystalline polymers. The selective formation of highly oriented polymers in radical polymerisation is promoted by the preliminary structural organisation of the medium in which the process is carried out, which may be achieved by applying a magnetic field or by the fixation of the monomeric liquid-crystal structure.

Fig. 29 presents the diffraction patterns for polymers obtained by the radical polymerisation of acryloyloxybenzoic acid in the liquid crystal phase (curve *1*) and in isotropic solution in heptyloxybenzoic acid (curve *2*).[84] Curve *1* is characterised by a series of sharp diffraction maxima. The degree of crystallinity of the polymer is 40% according to X-ray diffraction data, while polymerisation in solution leads to the formation of a polymer with an amorphous structure.

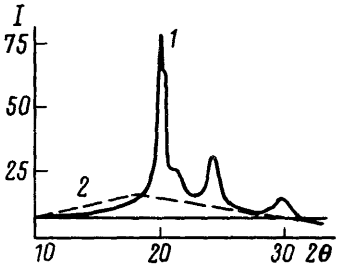


Figure 29. Diffractometer traces for polyacryloyloxybenzoic acid specimens obtained in the radical polymerisation of heptyloxybenzoic acid in bulk (curve *1*) and in solution in the monomer (curve *2*).

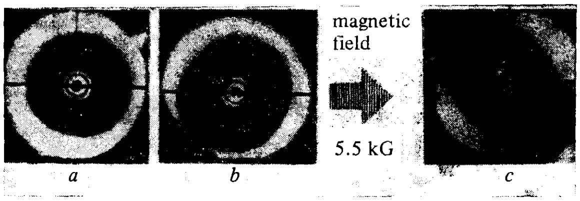


Figure 30. X-Ray diffraction patterns for the polymer of 4-n-hexyloxyphenyl 4′-acryloyloxybenzoate obtained by polymerisation from the isotropic phase (*a*), the liquid-crystal phase (*b*), and the liquid-crystal phase with application of a 5.5 G permanent field (*c*).

In the polymerisation of 4-n-hexyloxyphenyl 4′-acryloyloxybenzoate it was possible to obtain polymers with a high degree of orientation of the macromolecules by employing the intrinsic orientation order in the liquid crystal phase of the monomer as well as a magnetic field of 5.5 kG.[85] X-Ray diffraction patterns for the polymer obtained by radical polymerisation from the isotropic phase (*a*), the liquid-crystal phase (*b*), and the liquid-crystal phase with application of a steady magnetic field (*c*) are presented in Fig. 30.[85] The presence of denser regions on the diffraction rings indicates an increase in the anisotropy (degree of axial orientation of the macromolecules) of the specimens on passing from *a* to *c*. The polymer formed exhibits only axial orientation.

Magnetic and electric fields make it possible to influence the microstructures of polymeric specimens. Fig. 31 illustrates the changes in the isomeric composition of polybutadiene on polymerisation of butadiene under the influence of a magnetic field with the specimen (20% of butadiene in benzene) irradiated by ultraviolet light[86]. Dibenzothiazolyl sulphide was used as the sensitiser. Evidently, the polybutadiene obtained by polymerisation in the absence of a field contains ~30% of the *trans*-1,4-form. When a 5 kG magnetic field is applied, the content of *trans*-1,4-polybutadiene increases to 50%.

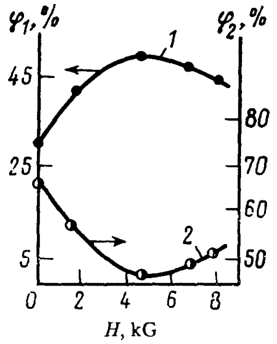


Figure 31. The influence of the magnetic field on the microstructure of polybutadiene formed on photochemical polymerisation at 25°C; sensitiser—dibenzothiazolyl sulphide (φ_1 and φ_2 are the yields of *cis*- and *trans*-polybuta-1,4-dienes).

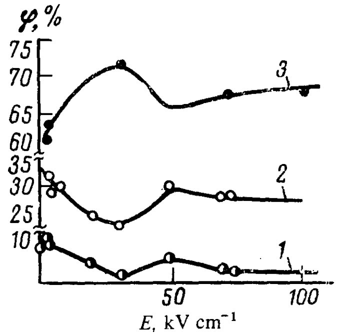


Figure 32. The contents of isotactic (curve *1*), heterotactic (curve *2*), and syndiotactic (curve *3*) triads in the polymerisation of methyl methacrylate in a permanent electric field at 60°C; initiator—azobisisobutyronitrile.

The mechanism of the phenomenon apparently includes the formation of an intermediate complex of the isomerising molecules with the free radical produced on photolysis of the sensitiser. The C=C bonds in the *trans*-position in the complex are ruptured and there are singlet–triplet transitions in the radical pairs. The role of the magnetic field is additional removal of the singlet–triplet degeneracy of the Zeeman interaction energy and an increase in the probability of the *cis–trans* isomerisation through the triplet state via an adiabatic pathway.

The application of a permanent electric field, like that of a magnetic field, can influence strongly the tacticity of the poly(vinyl acetate) formed in the polymerisation reaction[87]. Fig. 32 illustrates the influence of the electric field on the stereoregularity of the poly(vinyl acetate) formed by radical polymerisation in the presence of azobisisobutyronitrile as the radical initiator at 60°C. A sharp increase of the tacticity of the polymer is seen at an electric field strength of ~ 30 kV cm^{-1}.

The above examples suggest that magnetic and electric fields are promising factors whereby the selectivity of polymerisation processes may be influenced.

6. Thermodynamic Properties of the Monomer and the Formation of the Crystal Structure of the Polymer

Changes in the thermodynamic properties of monomer solutions (concentration, solvent, and temperature) may alter the crystal structure of the resulting polymer. At high concentrations of the monomer (for example, trioxan) macromolecules with a high molecular weight are formed in solution.

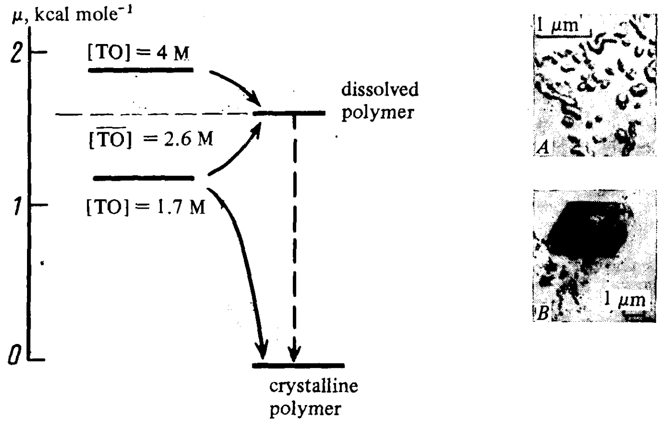


Figure 33. Thermodynamics of the polymerisation of trioxan; *A* and *B*—specimens of crystals formed on crystallisation of trioxan from solutions with [TO] > [$\overline{TO}$] and [TO] < [$\overline{TO}$]; {[$\overline{TO}$] = 2.6 M}.

Fig. 33 shows that the thermodynamic potential of trioxan (TO) in methylene chloride at a concentration of 4 M exceeds that of the polyformaldehyde macromolecule in this medium. The final product is formed in two stages—the macromolecule is formed initially and this is followed by its crystallisation from solution. At low concentrations of the monomer its thermodynamic potential is lower than that of the dissolved polymer molecule. The polymer molecules formed do not dissolve as the chain length increases and give rise to the solid crystalline phase almost immediately. Because of this, a cryptocrystalline polymer is formed in the former case, while in the latter case large crystals are produced (Fig. 33).[88,89]

The thermodynamic potentials of the polymer and the monomer also vary under the influence of temperature and the nature of the solvent.

Thus there are new possibilities for a thermodynamic approach to the regulation of the supermolecular structure of the polymer. The reaction is carried out under conditions close to the polymer ⇌ monomer equilibrium position. It is found that the formation of a polymer with an undesirable structure is thermodynamically impossible under these conditions.

7. Polymerisation Under the Influence of Shock Waves

The usefulness of shock waves in polymerisation reactions of many organic compounds has been demonstrated in recent years[90]. When a shock wave passes through solid organic monomers, even substances which do not undergo polymerisation under the usual conditions do polymerise (for example, benzene)[91]. The reaction is carried out in special "storage containers", the design of which makes it possible to protect substances subjected to compression by shock waves from decomposition (Fig. 34). Under these conditions, polymerisation is observed only at shock wave pressures exceeding a threshold value. The degree of reaction during the passage of the shock wave and the threshold polymerisation amplitude depend on the nature of the monomer.

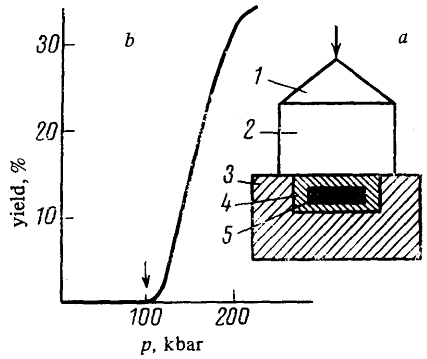


Figure 34. *a*) Schematic illustration of polymerisation under the influence of a shock wave: 1) generator of a planar detonation wave; 2) explosive; 3) housing; 4) container; 5) monomer; 6) dependence of the yield of polyacrylamide on the shock wave pressure. The arrow indicates the threshold pressure.

The use of shock waves makes it possible to obtain polymers with a much higher molecular weight than in the usual polymerisation. Thus, in the polymerisation of trioxan in a shock wave, the molecular weight of the polymer reaches 1.3×10^6, while in catalytic polymerisation it is 10^5. Depending on the conditions, polymerisation in a shock wave makes it possible to synthesise polymers with different structures.

The mechanisms of polymerisation in a shock wave cannot be reduced to a simple combination of compression and heating and apparently involves a new specific type of influence. The application of shock waves may be regarded as one of the possible factors for increasing process selectivity.

VIII. RADICAL PROCESSES IN THE CRACKING OF HYDROCARBONS

The selectivity in the formation of products in the cracking of hydrocarbons is determined by their structure. In paraffins and isoparaffins the difference between the energies of primary, secondary, and tertiary C–H bonds is as a rule small (390–410 kJ mole^{-1}). The energy of the C–C bond is virtually constant along the hydrocarbon skeleton (330–340 kJ mole^{-1}), its value being slightly higher only for the abstraction of terminal methyl groups (350–360 kJ mole^{-1}).[92] For this reason, the process at low temperatures (up to 500°C) is non-selective and leads to the formation of a wide range of products, for example[92a]:

$$\text{(0)} \quad CH_3{-}CH_2CH_2{-}CH_3 \rightarrow 2C_2H_5^{\cdot},$$

$$\text{(0')} \quad CH_3{-}CH_2CH_2{-}CH_3 \rightarrow CH_3^{\cdot} + C_3H_7^{\cdot},$$

$$\text{(2.1)} \quad C_2H_5^{\cdot} + C_4H_{10} \rightarrow C_2H_6 + C_4H_9^{\cdot},$$

$$\text{(2.2)} \quad CH_3^{\cdot} + C_4H_{10} \rightarrow CH_4 + C_4H_9^{\cdot},$$

$$\text{(2.3)} \quad C_3H_7^{\cdot} + C_4H_{10} \rightarrow C_3H_8 + C_4H_9^{\cdot},$$

$$\text{(2.4)} \quad C_2H_5^{\cdot} \rightarrow H^{\cdot} + C_2H_4,$$

$$\text{(2.5)} \quad C_3H_7^{\cdot} \rightarrow CH_3^{\cdot} + C_2H_4,$$

$$\text{(2.6)} \quad H^{\cdot} + C_4H_{10} \rightarrow H_2 + C_4H_9^{\cdot},$$

$$\text{(2.7)} \quad CH_3{-}\dot{C}H{-}CH_2CH_3 \rightarrow C_3H_6 + CH_3^{\cdot},$$

$$\text{(2.8)} \quad \dot{C}H_2{-}CH_2{-}CH_2CH_3 \rightarrow C_2H_4 + C_2H_5^{\cdot},$$

$$C_2H_5^{\cdot},\ C_3H_7^{\cdot},\ C_4H_9^{\cdot} \rightarrow \text{chain termination.}$$

1. The Influence of Temperature and Reactant Concentrations on Selectivity in Cracking

It is seen from the overall cracking mechanism that free radicals are transformed via several pathways in the chain propagation stages: unimolecular decomposition via reactions (2.4) and (2.5) and bimolecular interaction with the initial substance via reactions (2.1) and (2.3). Individual elementary stages are characterised by different activation energies, so there is the possibility, in principle, of altering the ratios of the rates of parallel elementary stages by changing the temperature (the selectivity is influenced via the value of α).

In the cracking of butane, the processs selectivity is determined by the competition between reactions (2.4) and (2.5), which lead to the formation of ethylene, and between reactions (2.1) and (2.3), which lead to the accumulation in the system of low-molecular-weight alkanes as side products. Table 10 presents the rate constants for these elementary stages[92].

The rate ratios $w_{2.4}/w_{2.1}$ and $w_{2.5}/w_{2.3}$, calculated using the above constants, increase with temperature and, when $t > 800$°C and the butane concentration in the gas phase $[C_4H_{10}] \simeq 10^{-3}$ mole cm^{-3}, the rate of the unimolecular decomposition of alkyl radicals is significantly greater than the rates $w_{2.1}$ and $w_{2.3}$ of the bimolecular conversion of $C_2H_5^{\cdot}$ and $C_3H_7^{\cdot}$ respectively. A decrease in the concentration of butane (for example, by diluting it with an inert gas) decreases the temperature at which the conditions $w_{2.4} > w_{2.1}$ and $w_{2.5} > w_{2.3}$ hold. Thus it is possible to increase the selectivity in the cracking of butane to ethylene by raising the temperature and by diluting butane with an inert gas. This procedure is used in industry, where pyrolytic processes, designed to obtain ethylene, are carried out at high temperatures and with dilution by steam.

Table 10. The rate constants for the chain propagation reactions in the cracking of butane.

Reaction	lg k_0 (cm^3 mole^{-1} s^{-1})	E, kJ, mole^{-1}	Reaction	lg k_0 (cm^3 mole^{-1} s^{-1})	E, kJ, mole^{-1}
(2.1)	2.0	42	(2.4)	14.2	126
(2.3)	9.8	40	(2.5)	15.4	142

2. Coupled Cracking. Transfer of the Reaction to a New Pathway

The transfer of the reaction to a new chain pathway by coupling processes makes it possible to alter the nature and activity of the radicals propagating the main chain and hence the selectivity in the cracking process. This principle has been used to increase the selectivity in the cracking of piperylene. At 650–700°C the cracking of piperylene proceeds with formation of cyclopentadiene (the selectivity $S_c \simeq 30$ mole % relative to the unconsumed piperylene) and butadiene ($S_b = 50$ mole %) (Table 11) and involves the mechanism[93]

$$C_5H_8 \rightarrow C_5H_7^{\cdot} + H,$$

$$\text{(1.1)} \quad C_5H_7^{\cdot} + C_5H_8 \xrightarrow{k_{1.1}} C_5H_9^{\cdot} + C_5H_6,$$

$$\text{(2.1)} \quad H^{\cdot} + C_5H_8 \xrightarrow{k_{2.1}} C_5H_9^{\cdot},$$

$$\text{(0.1)} \quad C_5H_9^{\cdot} \xrightarrow{k_{0.1}} CH_3^{\cdot} + C_4H_6 \ \text{(butadiene)},$$

$$\text{(3.1)} \quad CH_3^{\cdot} + C_5H_8 \xrightarrow{k_{3.1}} C_5H_7^{\cdot} + CH_4,$$

$$(CH_3^{\cdot},\ C_5H_9^{\cdot},\ C_5H_7^{\cdot}) \rightarrow \text{chain termination.}$$

The introduction of hydrogen into the reaction causes the replacement by hydrogen atoms of the $CH_3^{\cdot}$ radicals whose subsequent transformation leads to the formation of cyclopentadiene. As a result, the unit of the cracking chain consisting of the sequence of reactions (1.1), (0.1), and (3.1) is replaced by the sequence of reactions (2.1), (0.1), and (3.2):

$$\text{(3.2)} \quad CH_3^{\cdot} + H_2 \xrightarrow{k_{3.2}} CH_4 + H\ .$$

Table 11. The selectivity in the cracking of piperylene.

System	S_c, mole %	S_b, mole %	System	S_c, mole %	S_b, mole %
In the absence of H_2	30	50	In the presence of added H_2	10	70

This change in the pathway increases the process selectivity with respect to butadiene (Table 11). When account is taken of the reaction involving chain transfer by $CH_3^{\cdot}$

radicals [reaction (3.2)], the above mechanism of the cracking of piperylene makes it possible to obtain expressions for the integral selectivity S_b in the formation of butadiene.

According to Eqn.(2a), the differential selectivity in the formation of butadiene is

$$\sigma_{C_4H_6} = \frac{k_{0.1}[C_5H_9^{\cdot}]}{k_{1.1}[C_5H_7^{\cdot}] + k_{2.1}[H] + k_{3.1}[CH_3^{\cdot}]} \quad . \tag{21}$$

By expressing the concentrations of all the active centres in terms of the concentration of $CH_3^{\cdot}$ radicals and assuming that the chain is long, we find

$$[C_5H_7^{\cdot}] = k_{3.1}[CH_3^{\cdot}]/k_{1.1};\ [H^{\cdot}] = \frac{k_{3.2}[H_2]}{k_{2.1}[C_5H_8]}[CH_3^{\cdot}];$$

$$[C_5H_9^{\cdot}] = \frac{k_{3.1}[C_5H_8] + k_{3.2}[H_2]}{k_{0.1}}[CH_3^{\cdot}] \quad .$$

On substituting the values obtained in Eqn.(21), we obtain an expression relating the differential selectivity with respect to butadiene to the concentrations of the initial substances C_5H_8 and H_2:

$$\sigma_{C_4H_6} = (k_{3.1}[C_5H_8] + k_{3.2}[H_2])/(2k_{3.1}[C_5H_8] + k_{3.2}[H_2]) \quad .$$

In the absence of hydrogen S_b is independent of C and is equal to 0.5. As the hydrogen concentration increases, the differential process selectivity rises from 1/2 to 1. There is a corresponding change also in the integral selectivity. In the presence of hydrogen

$$S_b(C) = \frac{1}{2}\left[1 - \frac{k_{3.2}[H_2]_0}{2k_{3.1}[C_5H_8]_0 C}\ln\left(1 - \frac{2k_{3.1}[C_5H_8]_0 C}{k_{3.2}[H_2]_0 + 2k_{3.1}[C_5H_8]_0}\right)\right] .$$

With increase of the degree of conversion, S_b changes from

$$S_b = \frac{1}{2}\left(1 - \frac{k_{3.2}[H_2]_0}{k_{3.2}[H_2]_0 + 2k_{3.1}[C_5H_8]_0}\right)$$

for very low degrees of cracking ($C \to 0$) to

$$S_b = \frac{1}{2}\left(1 - \frac{k_{3.2}[H_2]_0}{2k_{3.1}[C_5H_8]_0}\ln\left[1 - \frac{2k_{3.1}}{k_{3.2}}\left(\frac{[H_2]_0}{[C_5H_8]_0} + \frac{2k_{3.1}}{k_{3.2}}\right)^{-1}\right]\right)$$

for the degree of conversion $C = 1$. For example, calculation showed that, for the rate constant ratio $2k_{3.1}/k_{3.2} = 0.5$ and an equimolar mixture of piperylene and hydrogen $\{[H_2]_0/[C_5H_8]_0 = 1\}$, the process selectivity $S_b = 0.85$, while in the absence of hydrogen $S_b = 0.5$ regardless of the degree of conversion of the hydrocarbon, since both products—butadiene and cyclopentadiene—are formed simultaneously in the first stage of the chain unit [reaction (1)] when $[H_2O]_0 = 0$. Thus in the presence of added hydrogen there is an increase also of the integral process selectivity with respect to butadiene. This result is consistent with the data in Table 11. Consequently the procedure involving the introduction of hydrogen makes it possible to increase the process selectivity S_b with respect to butadiene and to decrease the selectivity S_c with respect to cyclobutadiene. The selectivity with respect to cyclobutadiene may be increased by introducing hydrogen atom acceptors (for example, HCl). In many instances the cracking of ethane coupled with the main process may be used as a source of hydrogen atoms.

The mechanism of the cracking of a toluene–ethane mixture[94] may be formulated in the following form:

$$H^{\cdot} + C_6H_5CH_3 \to CH_3^{\cdot} + C_6H_6,$$
$$CH_3^{\cdot} + C_6H_5CH_3 \to CH_4 + C_6H_5CH_2^{\cdot},$$
$$2C_6H_5CH_2^{\cdot} \to C_6H_5CH_2{-}CH_2C_6H_5,$$
$$C_2H_6 + C_6H_5CH_2^{\cdot} \to C_6H_5CH_3 + C_2H_5^{\cdot},$$
$$C_2H_5^{\cdot} \to C_2H_4 + H^{\cdot},$$
$$CH_3^{\cdot} + CH_3^{\cdot} \to C_2H_6.$$

The competitions between the fourth and fifth reactions determines the yield of biphenyl and that between the first two reactions determines the yield of benzene. Enrichment of the mixture in ethane leads to an increase in the concentration of hydrogen atoms and hence of the yield of benzene formed by the interaction of hydrogen atoms with toluene. The selectivity in the cracking of toluene to benzene increases (Table 12). The increase of the cracking selectivity with respect to styrene is association with the reactions

$$C_6H_5CH_2^{\cdot} + CH_3^{\cdot} \to C_6H_5C_2H_5 \to C_6H_5CH{=}CH_2 + H_2,$$
$$C_6H_5^{\cdot} + C_2H_4 \to C_6H_5C_2H_4^{\cdot} \to C_6H_5CH{=}CH_2 + H^{\cdot},$$
$$C_6H_5^{\cdot} + C_2H_3^{\cdot} \to C_6H_5CH{=}CH_2.$$

In the absence of ethane C_2H_4 and $C_2H_3^{\cdot}$ are not formed in appreciable amounts during the reaction.

Table 12. The selectivities in the formation of the main products of the coupled cracking of toluene (mole %; 840°C; contact time in flow system 0.1 s).

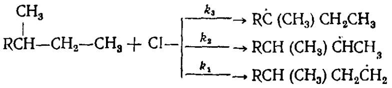
Cracking product	Toluene	43:57 toluene–ethane mixture (wt.%)	32:68 toluene–H_2 mixture (wt.%)
Benzene	45	70	98
Styrene and methylstyrene	13	20	1
Bibenzyl	20	2	—

IX. HALOGENATION OF HYDROCARBONS

The chlorination of hydrocarbons constitutes a sequence of chain reactions involving the chlorination of the initial hydrocarbon and its various chloro-derivatives formed during the process. The hydrocarbon chlorination processes have as a rule a low selectivity and proceed via the mechanism[95,96]

$$Cl_2 \to 2Cl^{\cdot},$$
$$RCH_3 + Cl^{\cdot} \to RCH_2^{\cdot} + HCl,$$
$$RCH_2^{\cdot} + Cl_2 \to RCH_2Cl + Cl^{\cdot},$$
$$RCH_2^{\cdot} + HCl \to RCH_3 + Cl^{\cdot},$$
$$RCH_2Cl + Cl^{\cdot} \to RCH_2^{\cdot} + Cl_2,$$
$$Cl^{\cdot} + Cl^{\cdot} + M \to Cl_2 + M,$$
$$Cl^{\cdot} + RCH_2^{\cdot} \to RCH_2Cl,$$
$$RCH_2^{\cdot} + RCH_2^{\cdot} \to \text{molecular products},$$
$$Cl^{\cdot} \to \text{destruction on the wall},$$
$$RCH_2Cl + Cl_2 \to RCHCl_2^{\cdot} + HCl.$$

When there is a possibility of the parallel formation of several positional isomers in the system owing to the similar reactivities of the primary, secondary, and tertiary C–H bonds (390–410 kJ mole^{-1}), it is extremely difficult to alter the ratio of the isomers (and hence to increase the process selectivity with respect to one of the isomers, i.e. to alter the quantity $\alpha = k_i/\Sigma k_j$). The ratio of positional isomers as a rule assumes the statistical value. The small differences between the strengths of the primary, secondary, and tertiary C–H bonds in the hydrocarbon chain have almost no influence on the isomer ratio owing to the high reactivity of Cl atoms. However, the selectivity of the chlorination reaction may be significantly increased by carrying out the latter in solution and by reducing thereby the reactivity of chlorine atoms as a result of complex formation with the solvent. Chlorine atoms with a reduced reactivity are capable of "distinguishing" the C–H bonds in different positions, although the energies of the latter still do not differ greatly. The ratio of monochloro-derivatives (primary, secondary, and tertiary), formed at early stages in chain chlorination reactions, is determined by the rate constants for the reactions:



$$RCH(CH_3)-CH_2-CH_3 + Cl \xrightarrow{k_3} R\dot{C}(CH_3)CH_2CH_3;\quad \xrightarrow{k_2} RCH(CH_3)\dot{C}HCH_3;\quad \xrightarrow{k_1} RCH(CH_3)CH_2\dot{C}H_2$$

$$S_{-CH_2Cl} = k_1/(k_1+k_2+k_3),$$
$$S_{>CHCl} = k_2/(k_1+k_2+k_3),$$
$$S_{\geqslant CCl} = k_3/(k_1+k_2+k_3),$$

i.e. $S_{-CH_2Cl} : S_{>CHCl} : S_{\geqslant CCl} = k_1 : k_2 : k_3$.

It has been established experimentally that the use of different solvents, forming complexes with atomic chlorine and reducing its reactivity, leads to a greater process selectivity. Table 13 lists the rate constant ratios for the elementary steps in the interaction of chlorine atoms with C–H bonds in alkanes and aromatic alkyl-substituted hydrocarbons. Evidently, when the reaction is carried out in a solvent, the rate constant ratio increases sharply. The ratio k_3/k_1 for 2,3-dimethylbutane increases from 6 to 225 in CCl_4 (at 25°C) and from 3.7 to 18.4 (at 55°C) in anisole, i.e. when the reaction is carried out in a complex-forming solvent, the relative rate of the interaction of Cl with the t-C–H bond increases compared with the reaction involving the primary bond. There is a corresponding increase of the selectivity in the formation of 2-chloro-2,3-dimethylbutane. (In this calculation no account was taken of the possibility of further chlorination of the monochloro-derivatives.)

The regulating influence of the solvent increases with increase of its concentration owing to the shift of the equilibrium

$$Cl^{\cdot} + SH \rightleftarrows \dot{C}l \cdot SH$$

towards the formation of the complex.

Table 13. The relative rate constants for the abstraction by a chlorine atom of tertiary and primary hydrogen atoms from 2,3-dimethylbutane (k_3/k_1) and α- and β-hydrogen atoms from aromatic hydrocarbons (k_α/k_β) in chlorination by molecular chlorine at 55°C.[96]

Solvent	k_3/k_1	k_α/k_β		Solvent	k_3/k_1	k_α/k_β	
	2,3-dimethylbutane	ethylbenzene	cumene		2,3-dimethylbutane	ethylbenzene	cumene
Without solvent	3.7	14.5	42.2	Anisole	18.4	—	—
Without solvent	6.0*	—	—	Chlorobenzene	27.5*	—	—
t-Butyl alcohol	4.8	—	—	Benzene	49.0*	—	—
1,4-Dioxan	5.6	—	—	Carbon disulphide	225.0*	—	—
Nitrobenzene	4.9	2.7	5.2				

*Chlorination temperature 25°C.

1. Selectivity of the Halogenation Reaction at Low Temperatures

By carrying out the reactions at low temperatures, it is possible to obtain high selectivities because of the possibility of increasing the sensitivity of the reaction to the energetic parameters of different stages[97]. It is possible to obtain the desired product in a high yield even for very low differences between the activation energies for the main and side reactions (ΔE). For example, in the parallel reactions

$$A - \begin{cases} \xrightarrow{k_1} P_1\ (k_1 = k_{10}e^{-E_1/RT}), \\ \xrightarrow{k_2} P_2\ (k_2 = k_{20}e^{-E_2/RT}) \end{cases}$$

with $E_1 - E_2 = \Delta E$ = 3 kcal mole^{-1} (750 J mole^{-1}) and the pre-exponential factor ratio $k_{10}/k_{20} = 5$, the ratio of the selectivities in the formation of P_1 and P_2 is

$$\frac{S_{P_1}}{S_{P_2}} = \frac{k_1}{k_2} = \frac{k_{10}}{k_{20}} e^{-\Delta E/RT} = 5 \cdot e^{-3000/RT}.$$

At 300°C the ratio $S_{P_1}/S_{P_2} = 1.42$, so that $S_{P_1} = 0.59$ and $S_{P_2} = 0.41$ (the process is non-selective). In the same case at 100 K we have $S_{P_1}/S_{P_2} = 0.114$, $S_{P_1} = 0.10$, and $S_{P_2} = 0.90$, i.e. a high selectivity with respect to P_2 is achieved.

The wide-scale use of low temperatures has been retarded hitherto by the conviction that below 250 K the rates of chemical reactions are extremely low. However, studies in the last two decades have disproved this view. Many processes involving halogens occur at very high rates at 77–100 K, for example. Fig.35 shows that the liquid-phase chlorination of olefins at low temperatures is faster than in the gas phase. Even in the solid phase at ~100 K, the reaction proceeds at appreciable rates. The selectivity data for the reaction between ethylene and Cl_2 illustrated in Fig. 35 show that substitution processes are completely suppressed at low temperatures, i.e. processes involving the dissociation of the C–H bond are altogether absent and high quantitative yields of 1,2-addition products are obtained.

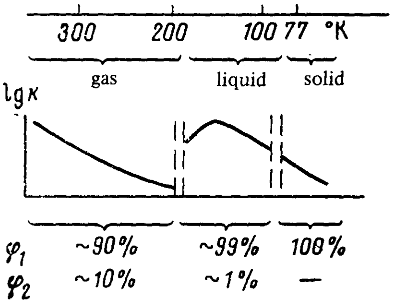


Figure 35. Chlorination of olefins in the gas phase, a supercooled liquid, and in the solid phase; k—rate constant for the dark reaction; φ_1 and φ_2—yields of addition and substitution products respectively.

The mechanism of the low-temperature reaction may be represented as follows:

$$C_2H_4 + Cl_2 \rightleftarrows C_2H_4 \cdot Cl_2 \quad (\Delta H \leqslant 10\ \text{kJ mole}^{-1}),$$

this being followed by the molecular rearrangement

$$C_2H_4 \cdot Cl_2 \rightarrow \quad \text{cyclic transition state} \quad \rightarrow C_2H_4Cl_2$$

and the chain process

$$C_2H_4{\cdot}Cl_2 \rightarrow C_2H_4Cl^{\cdot} + Cl^{\cdot} \rightarrow C_2H_3Cl + HCl.$$

The selective course of the process is associated with the involvement in the reactions of molecular complexes capable of a synchronous rearrangement under certain conditions to the reaction products or active radical species. The chain mechanism of the process at low temperatures is to a large extent suppressed owing to energy-dependent selectivity (based on the differences between the activation energies). When the low-temperature reaction is carried out in a solvent with pronounced complex-forming properties (HCl), the radical-chain component can be almost completely suppressed.

In liquid HCl, the process develops via the mechanism

$$Cl_2 + HCl \rightleftarrows Cl_2{\cdot}HCl,$$
$$Cl_2{\cdot}HCl + C_2H_4 \rightleftarrows (C_2H_4{\cdot}Cl_2{\cdot}HCl) \rightarrow C_2H_4Cl_2 + HCl.$$

Its activation energy is $E = 10-20$ kJ mole^{-1}.

The yield of the 1,2-dichloro-derivative is limited by the purity of the reactants and may be raised to 100%. In reactions with participation of halogens in non-polar media a negative temperature coefficient is frequently obtained. This effect can be accounted for by the occurrence of rapid reversible stages, in particular, complex formation stages. The activation energy for a consecutive reaction

$$A + B \overset{K}{\rightleftarrows} A{\cdot}B \xrightarrow{k} P,$$

where $K = K_0e^{-\Delta H/RT}$ ($\Delta H < 0$) and $k_0e^{-E/RT}$ ($E > 0$), is the sum of the positive activation energy E and the negative enthalpy of complex formation ΔH: $E_{obs} = E - |\Delta H|$. If $|\Delta H| > E$, a negative temperature coefficient is observed. The reaction proceeds with acceleration as the temperature is reduced to a value T_{max}, after which the rate begins to fall. The relation between T_{max} and E and ΔH is given by the equation

$$\frac{1}{T_{max}} = \frac{4.57}{|\Delta H|} \lg\left(\frac{|\Delta H| - E}{E}\right) + \frac{\Delta S}{|\Delta H|}.$$

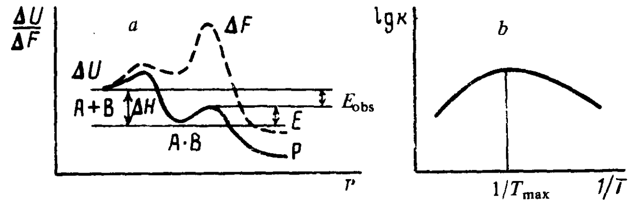
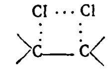


Figure 36. *a*) Reaction pathway characterised by a negative temperature coefficient (continuous line) and variation of ΔF in this process (dashed line); *b*) temperature variation of the rate constant for the reaction proceeding via the formation of a complex; T_{max} corresponds to complete binding of the components in the complex.

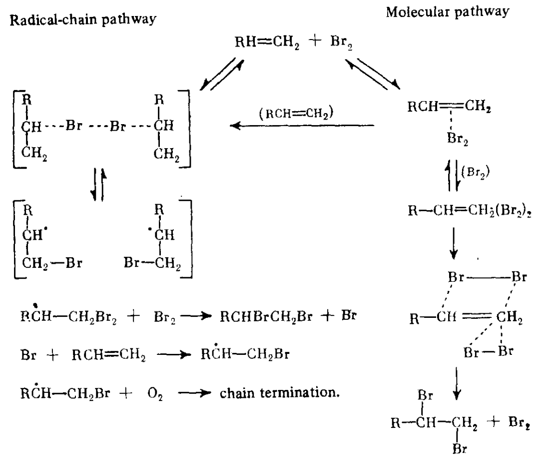
Fig. 36 illustrates the "energy–reaction pathway" scheme for a process with $E_{obs} < 0$ (the activation energy E_{obs} is an effective value). The reaction proceeds via this pathway when the complex AB (Fig. 36) is converted into the product via a cyclic transition state, for example



in the chlorination of olefins.

A high negative activation entropy is characteristic of processes of this kind, as a result of which the potential energy well for this type of transition state lies below the energy level of the initial molecules and $E_{obs} < 0$. When the temperature is reduced rapidly, the reactants are completely bound in an extremely stable complex AB. Many systems are known for which negative values of E_{obs} have been found: chlorine–olefin, bromine–olefin, iodine chloride and bromide–olefins, bromine–α-hydroxycyclopropanes, bromine–arylcyclopropanes, NOCl–epoxides, etc. The values of E_{obs} for the above processes are in the range between 0 and 60 kJ mole^{-1} and the maximum rate of the process is reached at 230–170 K. Thus there is a possibility of carrying out many reactions at high rates even at very low temperatures. Cryochemistry leads to new possibilities for selective reaction conditions.

In reality the interpretation of the nature of the negative temperature coefficient in halogenation is more complex[97]. At low temperatures energy-dependent selectivity is accompanied also by selectivity based on mechanisms in principle associated with the energetics of parallel reactions. The bromination of olefins at room temperature takes place simultaneously via two pathways:



$$R\dot{C}H{-}CH_2Br_2 + Br_2 \longrightarrow RCHBrCH_2Br + Br$$
$$Br + RCH{=}CH_2 \longrightarrow R\dot{C}H{-}CH_2Br$$
$$R\dot{C}H{-}CH_2Br + O_2 \longrightarrow \text{chain termination.}$$

The process may proceed via a synchronous rearrangement of the 2 : 1 bromine-olefin complex (molecular pathway). The existence of such complexes has been demonstrated experimentally and their structure has been confirmed by quantum-mechanical calculations. The rate in the molecular olefin transformation pathway is

$$w_m = k'[RCH{=}CH_2][Br_2]^2 \quad (E'_{obs} = -15 \div -30 \text{ kJ mole}^{-1}) \; .$$

On the other hand, the synchronous process involving the dissociation and formation of bonds in the complex may lead to the formation of radicals (the radical-chain pathway). The rate in the radical-chain pathway is

$$w_c = k[RCH{=}CH_2]^2[Br_2]^2.$$

The mechanism of the chain process involves reversible stages, for example, the reaction of bromine atoms with an olefin molecule:

$$Br + CH_2{=}CHR \rightleftarrows [Br{\cdot}CH_2{=}CHR].$$

For this reason, a negative temperature coefficient is also observed in the radical-chain reaction and is greater than in the molecular reaction. Depending on the nature of the group R, the activation energy E_{obs} varies from -20 to -60 kJ mole^{-1}. The ratio of the rates in the radical-chain and molecular pathways of the reaction with olefins is proportional to the olefin concentration:

$$w_c/w_m = (k/k') \cdot [\mathrm{RCH{=}CH_2}].$$

The two processes give rise to different products (Table 14). By reducing the temperature and increasing the olefin concentration, it is possible to isolate the radical pathway, while the addition of inhibitors makes it possible to isolate the molecular pathway. Thus by altering the experimental conditions, one can isolate selectively the different pathways in the low-temperature halogenation reactions. Table 14 presents as an example data for the bromination of hex-1-ene. Analogous results were obtained in the chlorination of olefins and in reactions of halogens with epoxides and arylcyclopropanes.

Table 14. Hex-1-ene bromination products at 300 K (% of sum of products formed via a given pathway).

Product	Molecular pathway	Radical pathway
$\mathrm{CH_2BrCHBr(CH_2)_3CH_3}$	97	50
$\mathrm{CH_2BrCH{=}CH(CH_2)_2CH_3}$	3	34
$\mathrm{CH_2{=}CH{-}CH{-}Br(CH_2)_2CH_3}$	—	12
$\mathrm{CHBr{=}CH(CH_2)_3CH_3}$	—	4
$\mathrm{CH_2{=}CBr(CH_2)_3CH_3}$		

The pathways in the low-temperature reactions can be additionally regulated by introducing complex-forming additives or solvents into the system. A high selectivity in additive chlorination has been noted when the reaction was carried out in liquid HCl. The role of the additive usually reduces to binding electron-accepting species (halogen atoms and molecules) in a complex, reducing their electrophilic properties, and increasing the process

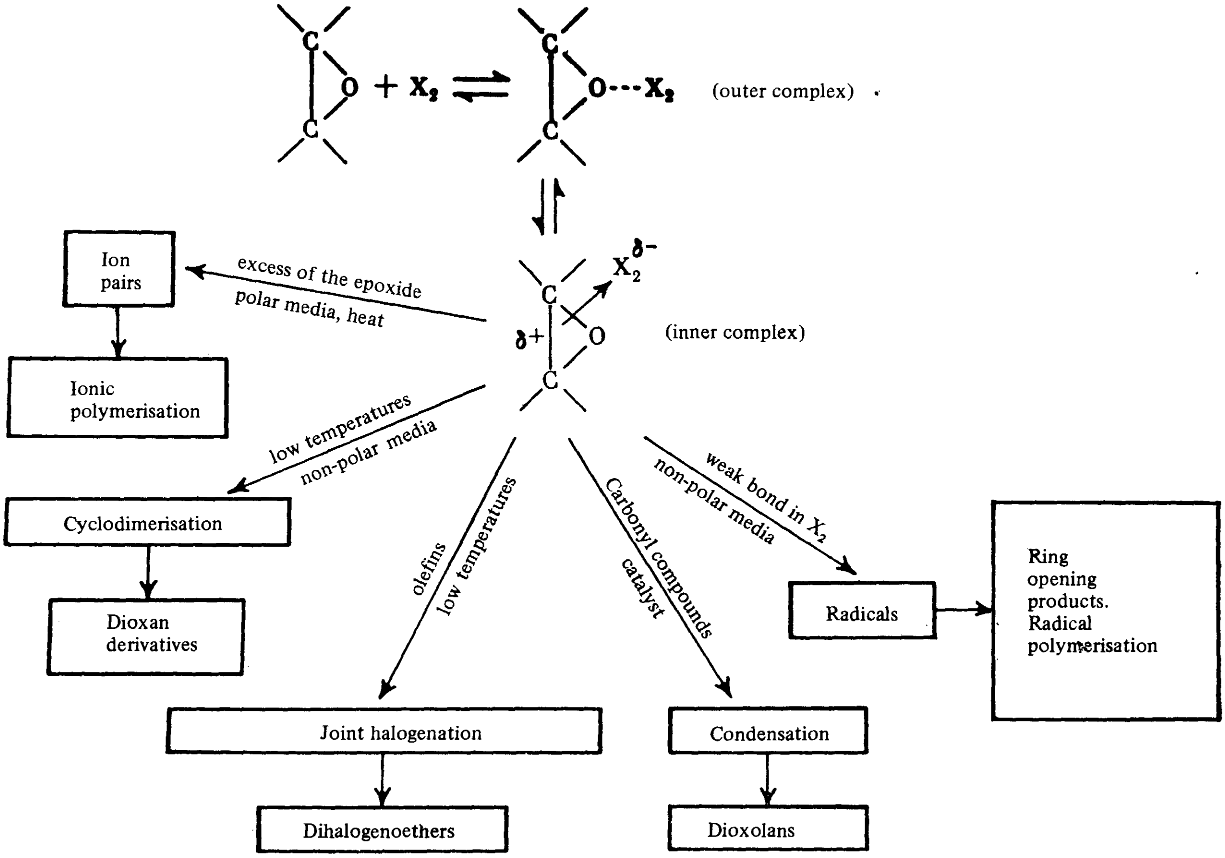


Figure 37. Reaction pathways in the halogen (X_2)—epoxide system.

selectivity. Selection based on different mechanisms can be achieved with the aid of complex-forming agents. Thus the addition of electron-donating compounds in the bromination of hex-1-ene suppresses the radical-chain pathway and makes it possible to obtain selectively the 1,2-addition product. The role of complex formation in energy-dependent selection was examined by Russell[98] as early as the 1960s. At low temperatures, where the energy-dependent selection is manifested most strikingly, these effects become particularly appreciable. When additive and substitutional chlorination of alkanes and chloroalkanes is carried out at 200–230 K in the presence of, for example, aromatic additives, 100% selectivity may be achieved.

The reactions of halogens with epoxides involve complex formation at the obligatory initial stage. Subsequent reaction of the complex proceeds via different pathways depending on the conditions: ionic polymerisation, molecular cyclodimerisation, and a radical-chain reaction involving the opening of the epoxide ring. In the presence of a third component (olefin, carbonyl compound, etc.) there is also a possibility of competition between the ionic, molecular, and radical mechanisms[99,100] (see the scheme in Fig. 37).

By varying the temperature and experimental conditions within wide limits, it is possible to isolate the molecular, radical, or ionic pathway in the halogenation reaction virtually in any system and hence one can obtain the product or the sum of products corresponding to only one of the possible pathways.

On transition of the system from the liquid to the frozen state, a new effective factor becomes available for controlling the rate and mechanism of the chemical reaction.

2. Catalytic Chlorination of Hydrocarbons

A common procedure for increasing the selectivity in radical reactions involves the introduction into the initiating systems of catalysts (organic or inorganic compounds), which behave as electron or ligand transferring agents. This approach does not always lead to the desired results, since the free radical in solution interacts not only with the catalytic transferring agent but also with other components of the medium.

A new approach to the solution of the problem of the selective synthesis of chloroalkanes involves carrying out the reactions under conditions where the reactants interact via the formation of radicals stabilised in the coordination sphere of a metal. It has been found that many halogen-containing iron compounds, where the metal ions exist in different oxidation states, for example hexakisacetonitrileiron(II) bis(tetrachloroferrate) $\{[Fe(II).(CH_3CN)_6][Fe(III)Cl_4]_2\}$, as well as other iron complexes, containing dimethylformamide or dimethyl sulphoxide as the neutral ligand, exhibit a high catalytic activity in the synthesis of chloroalkanes and make it possible to obtain different chloro-derivatives with a high selectivity[101]. The catalytic effect of dinuclear iron complexes has been demonstrated in chlorination by molecular chlorine, for example, in the reaction

and, when other chlorinating agents are used (for example, CCl_4):

$$CH_2{=}CH_2 + CCl_4 \rightarrow CCl_3(CH_2{-}CH_2)_nCl \quad \text{or}$$

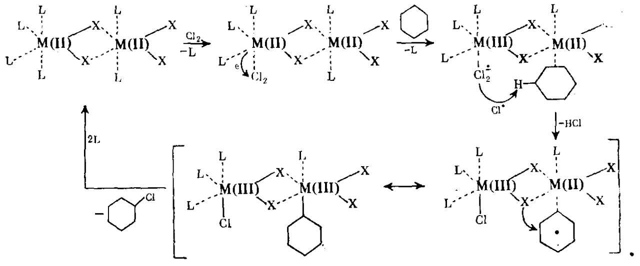
$$CH_2{=}CH{-}CH{=}CH_2 + CCl_4 \rightarrow CCl_3(CH_2{-}CH{=}CH{-}CH_2)_mCl \; .$$

Depending on the conditions under which it is synthesised and isolated and the conditions in the course of the catalytic reaction, the complex $[Fe(II)(CH_3Cl)_6][Fe(III)Cl_4]_2$ undergoes an intramolecular electronic transition, which leads to the formation of two different forms of Fe(II):

$$[Fe(II)L_6]\cdot[Fe(III)X_4]_2 \rightleftarrows [Fe(III)L_6]\cdot[Fe(II)X_4]\cdot[Fe(III)X_4] \rightleftarrows$$
$$\rightleftarrows [Fe(II)L_6] + [Fe(III)L_6] + [Fe(II)X_4] + [Fe(III)X_4] \; ,$$
$$[Fe(II)X_4] + [Fe(II)L_6] \rightleftarrows [Fe(II)L_6]\cdot[Fe(II)X_4] \; ,$$
$$[Fe(II)L_6][Fe(II)X_4] \rightleftarrows L_4Fe(II)X_2Fe(II)L_2X_2 \; ,$$
$$(X{=}Cl;\ L = CH_3CN;\ (CH_3)_2NCHO;\ \text{or}\ (CH_3)_2SO) \; .$$

In the presence of catalysts containing at least two Fe(II) atoms the chlorination reactions proceed via the intermediate formation of the radical-anions $Cl_2^{\overline{\cdot}}$ and $CCl_4^{\overline{\cdot}}$ in the coordination sphere of the metal.

After the transfer of the ligand to the substrate (cyclohexane, ethylene, and butadiene) coordinated to a neighbouring metal atom or after the elimination of a hydrogen atom, the reactions proceed via the formation of a metal–carbon bond or a radical resonance-stabilised in the coordination sphere of the metal. The close proximity of the reacting species in the coordination sphere of a dinuclear bridge complex increases sharply the process selectivity or leads to the appearance of new chlorination pathways. Thus, in the chlorination of cyclohexane the selectivity in the formation of the monochloro-derivative via the radical-chain mechanism does not exceed 80 mole %. In the presence of catalysts of the above type the selectivity in the formation of cyclohexyl chloride reaches 98–99 mole %.[101] The process involves the formation of $C_6H_{11}^{\cdot}$ radicals, bound in a complex, via the mechanism

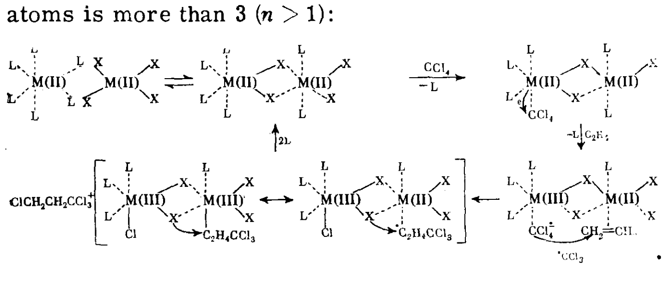


The chlorination of ethylene by carbon tetrachloride involves the reaction

$$CH_2{=}CH_2 + CCl_4 \rightarrow CCl_3(CH_2CH_2)_nCl$$

in which products with $n = 1$, 2, and 3 are formed.

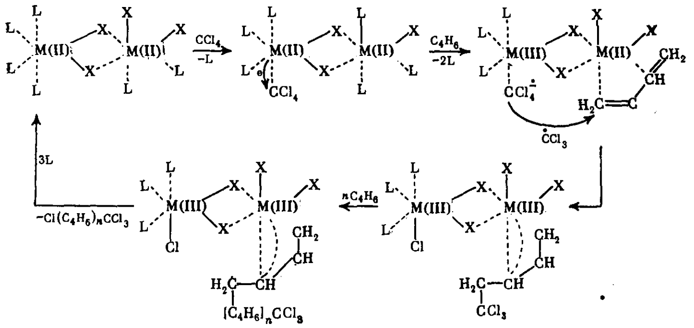
The use of a catalyst makes it possible to increase the selectivity in the formation of 1,1,1,3-tetrachloropropane ($n = 1$) from 30 to 95%. The catalytic process takes place in the coordination sphere of the metal, preventing the formation of isomers in which the number of carbon atoms is more than 3 ($n > 1$):



In the chlorination of butadiene[102] by CCl_4,

$$CH_2{=}CH{-}CH{=}CH_2 + CCl_4 \rightarrow Cl\,(CH_2CH{=}CHCH_2)_nCCl_3$$

the use of a catalyst leads to the formation of a chlorine-containing oligobutadiene—1,1,1,21-tetrachlorohenelcosane-3,7,11,15,19[$CCl_3(C_4H_6)_5Cl$, $n = 5$] with a selectivity of 95 mole %:



In the absence of the catalyst the above product is not formed at all.

It is seen from the examples quoted that the use of catalysts which propagate the process via an inner sphere mechanism in the coordination sphere of the metal constitutes an extremely effective procedure for altering the selectivity of chlorination reactions.

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The Structure and Reactivity of Phosphorus Pentachloride

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Data are presented on the reactions of phosphorus pentachloride with compounds containing oxa- and oxy-groups (ethers, acetals, oxetans, tetrahydrofuran, 1,3-dioxans, dioxolans, dihydropyrans, and alcohols). The structure of phosphorus pentachloride in various solvents and its influence on the course of reactions are considered. The mechanisms proposed for the reactions under discussion are analysed.

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I. INTRODUCTION

Interest in methods of synthesis of organophosphorus compounds containing a phosphorus–carbon bond is due to the practical importance of phosphonates and phosphinates and the development of theoretical ideas concerning the cause of the redistribution of old and the formation of new bonds.

The possibilities of phosphorylation with phosphorus pentachloride have been greatly expanded in recent years in connection with the use in this reaction of many ethers and a wide variety of oxa-compounds. A common feature of the latter reactions is that they proceed via a stage involving the formation of an α-halogeno-ether, which is capable of undergoing further dehydrochlorination. Definite advances have been achieved in the interpretation of the mechanisms of the interaction of phosphorus pentachloride with nucleophiles.

The history of the development of studies on the reactions of phosphorus pentachloride is described in Kabachnik's review[1] and has been supplemented by Pudovik and Khairullin[2].

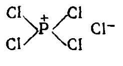
Thus the character of this review differs somewhat from that of the above publications and, apart from the description of syntheses, includes data on the structure of phosphorus pentachloride and the proposed mechanisms.

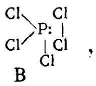
II. THE STRUCTURE OF PHOSPHORUS PENTACHLORIDE

In many cases the phosphorus atom is capable of expanding its valence shell, probably by employing vacant $3d$ orbitals. It is believed that the problem of the degree of involvement of d orbitals in σ and π bonds should be solved separately for each specific instance[3]. The hybridisation of s and p orbitals with d orbitals leads to several geometrical shapes which are determined by different angular functions of the d orbitals[4]. One of the possible forms is a bipyramidal dsp^3-hybrid structure[5].

Studies on phosphorus pentachloride in the vapour state by electron diffraction[6,7] indicate a trigonal bipyramid. Phosphorus pentachloride molecules in the liquid phase have a similar structure, which has been confirmed by conductimetric and Raman spectroscopic studies[8]. The spectra proved to be characteristic of molecules with a trigonal bipyramidal structure[9-11]. The bipyramidal sp^3d-hybrid structure is believed to be energetically the most favourable[5] for derivatives of five-coordinated phosphorus and has been confirmed by the existence of many covalent compounds in which the phosphorus atom is linked to five ligands: PF_5, PF_3Cl_2, PCl_5, $P(OC_6H_5)_5$, and $P(C_6H_5)_5$.[12-15]

However, the involvement of d orbitals in the formation of bonds is not indisputable and the problem still remains controversial. The ionisation potential of the s electron in the free atom is ~19 eV.[5] Calculations have shown that the energy evolved on formation of five P–Cl bonds is less than the excitation energy required for the transfer of $3s$ electrons to the $3d$ level[16]. Pauling[17] suggested that PX_5 molecules are stabilised by means of five resonance structures[17] of type A and six structures of type B:


A


B

The Cl–Cl bond in structure B is longer than the usual bond and its formation does not entail an appreciable decrease of molecular energy. According to Pauling's hypothesis, the five atoms in structure A are linked as a result of the hybridisation of the $3s$ and $3p$ orbitals and as a result of the electrostatic attractions between the P^+ ion and the single negative charge distributed between the five electronegative atoms. The energetic feasibility of the structure was demonstrated by Hudson[18] in relation to the formation of phosphorus pentachloride:

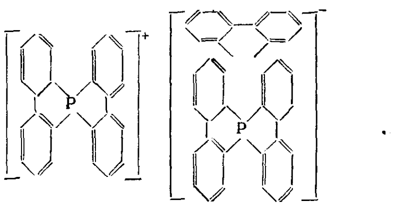
$$\ddot{P}Cl_3 \xrightarrow{-e} Cl_3P^{\dot{+}} \xrightarrow[-D_{P-Cl}]{Cl\cdot} Cl_4\overset{+}{P} \xrightarrow[-E_{Cl}]{e;+Cl\cdot} \overset{+}{P}Cl_4\overset{-}{Cl} \rightarrow Cl_4\overset{+}{P} \ldots \overset{-}{Cl} ,$$

where D_{P-Cl} is the dissociation energy and E_{Cl} the electrostatic interaction energy.

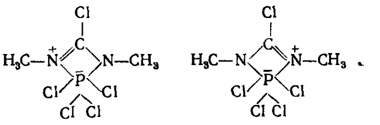
If it is assumed that $3d$ orbitals are involved in the formation of bonds in five-coordinated phosphorus compounds, then the formation of derivatives of six-coordinated phosphorus is also possible. This high valance is manifested in the PF_6^- and PCl_6^- ions corresponding to sp^3d^2 hybridisation[19,20]. Comparison of non-empirical calculations led Bochvar et al.[21] to the conclusion that the invocation of d orbitals in order to account for the electrophilic properties of phosphorus and the structure of its compound is not necessary. The authors believe that the bonds with axial ligands can be formed with participation of the p_z orbital of phosphorus and the atomic orbitals of the ligands, so that the hypothesis of the expansion of the valence shell of the phosphorus atom and of the existence of its sp^3d and sp^3d^2 valence states is not essential to account for the structure of phosphorus pentachloride and the PX_6^- anion. However, the conclusions in the above study[21] are not categorical; for this reason, we think it permissible to assume the involvement of *d* orbitals in bond formation.

The salt-like structure of phosphorus pentachloride has been confirmed by X-ray diffraction and by the determination of transport numbers in phosphorus pentachloride solutions in nitrobenzene[22,23]. According to ^{31}P NMR data, phosphorus pentachloride exists in the vapour state in a pentacovalent form (the chemical shift is +80 p.p.m.)[24]; in conformity with the ionisation hypothesis, two signals occur in a polar solvent: −91 p.p.m., which has been attributed to the $\overset{+}{P}Cl_4$ cation, and +281 p.p.m., attributed to the $\overset{-}{P}Cl_6$ anion. The phosphorus atom in the cation exists in the sp^3-hybrid state and the cation has a tetrahedral geometrical structure; the anion is a tetragonal bipyramid, which corresponds to sp^3d^2-hybridisation. The existence of tetrachlorophosphonium cations has been observed not only in the crystal lattice of phosphorus pentachloride but also in salt-like complexes, which have been examined by Horing and Baum[25] and studied in connection with ion transport in a nitrobenzene solution in the presence of aluminium trichloride and iron(III) chloride.[26,27] X-Ray diffraction analysis of crystalline compounds having the general composition $PCl_5.NbCl_5$ and $PCl_5.TaCl_5$, which showed that these compounds have heteropolar structures and consist of the $\overset{+}{P}Cl_4$ cation and the $NbCl_6$ and $TaCl_6$ anions respectively, led to the conclusion that the phosphorus is present in an ionic state[28].

The existence of phosphorus as a cation and an anion has been confirmed by an interesting reaction of phosphorus pentachloride with 2,2-dilithiobiphenyl and by a study of the resulting crystalline 'onium complex; the complex includes two phosphorus atoms with chemical shifts of −26.5 p.p.m. and +186.5 p.p.m.,[29] which corresponds to the structure:



X-Ray diffraction and ^1H and ^{31}P NMR spectra showed that the structure of the crystalline product [obtained by reaction of *N,N'*-dimethylchloroformamidine hydrochloride with PCl_5, $C_3H_6Cl_5N_2P$ (Ed. of translation)] with phosphorus in the six-coordinated state[30] may be represented by the formula



Thus, depending on the conditions, the phosphorus atom in PCl_5 may exist in both pentacovalent and ionic states. The nature of the structure is determined by external factors: the phase state, the type of solvent, and temperature. Thus it is believed that PCl_5 dissolved in carbon tetrachloride exists in a dimeric form while in methylene chloride it is monomeric[30-32]. It has been found[33] that PCl_5 in carbon tetrachloride is monomeric, the distortion being caused by the formation of associated species with the solvent. Analogous studies have been made for phosphorus halides R_nPX_{5-n} by NMR in solvents of different polarity and it has been concluded that these compounds have a pentacovalent structure in non-polar solvents[34]. The tendency to retain the pentacovalent structure falls in the sequence of substituents F > Cl > Br > I. Finally mention should be made also of the proposed structure (of the molecular complex type) of $PCl_3 \cdot Cl_2$, which is quite capable of existing under certain conditions: it has been detected for halides at a reduced temperature, but it is as a rule unstable on heating to room temperature[35-37].

Definite information about the structure of phosphorus halides is provided by nuclear quadrupole resonance (NQR). The ^{35}Cl NQR spectra of crystalline phosphorus pentachloride contain two groups of signals, which are similar within each group[37]. The NQR spectral frequencies quoted in the Table for phosphorus halides indicate the chemical non-equivalence of the chlorine atoms linked to phosphorus, which may be attributed to the non-equivalence of the axial and equatorial positions in the bipyramid[38]. The most bulky substituents occupy the equatorial positions, but this is probably not a general rule: thus the trichloromethyl groups is in the axial position. It is noteworthy that the structure of phosphorus pentabromide has not aroused controversy and is treated as ionic: $\overset{+}{P}Br_4\overset{-}{Br}$.[40] Phosphorus pentafluoride is treated as a pentacovalent compound[41].

The NQR spectra of phosphorus halides.

Compound	Transition frequency, MHz			Refs.
	$_{eq}P-Cl$	$_{ax}P-Cl$	C—Cl	
PCl_5	33,753; 33,753; 33,753	29,278; 29,245	—	38
$C_6H_5PCl_4$	33,446; 33,582	25,610; 25,512	—	38
CCl_3PCl_4	31,952; 29,458	28,250	39,689; 39,609; 39,749	39

III. PHOSPHORYLATION BY PHOSPHORUS PENTACHLORIDE OF COMPOUNDS WITHOUT MULTIPLE BONDS

1. Phosphorylation of Ethers

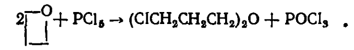
Reactions of these types have been discovered and investigated recently and are not included in the reviews quoted above. A series of studies on phosphorylation by phosphorus pentachloride was stimulated by the investigation of Petrov et al.[42], who demonstrated the possibility of the phosphorylation of ethers, and suggested that the reaction proceeds via a stage involving the formation of an α-halogeno-ether, which gives rise to a multiple bond on dehydrochlorination:

$$ROCH_2CH_3 + PCl_5 \xrightarrow{-HCl} [ROCHClCH_3 \xrightarrow{-HCl} ROCH{=}CH_2] + 2PCl_5 \rightarrow$$
$$\rightarrow [ROCHClCH_2PCl_3]^+ P\bar{C}l_6 \xrightarrow{SO_2} ROCH{=}CHP(O)Cl_2 + POCl_3 + SOCl_2 + HCl.$$

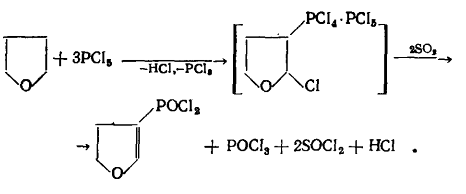
This was confirmed by a study of the reactions of phosphorus pentachloride with α-halogeno-ethers, which led to the isolation of the corresponding phosphonates[42-44].

2. Phosphorylation of Cyclic Oxa- and Dioxa-compounds

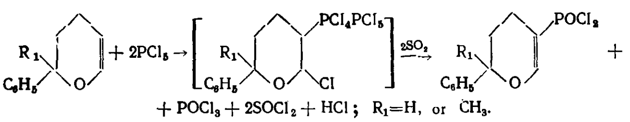
These reactions, which were carried out for the first time with four-membered cyclic compounds, did not make it possible to synthesise phosphorus-containing products. The reactions with oxetans terminated with formation of di-(γ-chloropropyl) ethers:



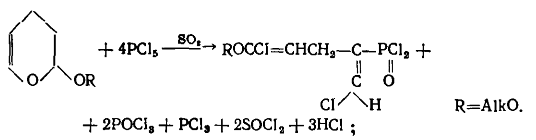
The reactions with tetrahydrofuran led to the synthesis of a phosphorylated product[45]:



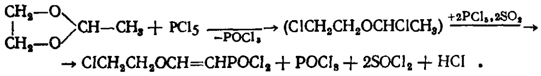
The reactions with dihydropyrans were also of the usual type:



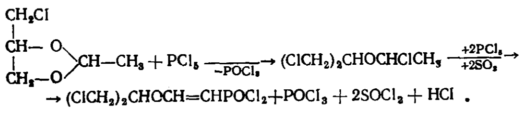
However, with R=AlkO the process occurred in such a way that the oxygen of the pyran ring was involved in the reaction, which was accompanied by consecutive chlorination and dehydrochlorination processes[46]:



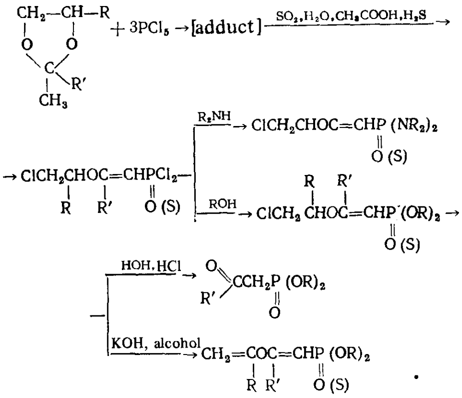
The first reactions with 4-methyl-1,3-dioxolan did not allow the isolation of products with a phosphorus–carbon bond[44]. On the other hand, a wide variety of derivatives of dioxolans and dioxans, containing substituents in the 2-position, led to phosphonates, confirming the general mechanism[47,48]:



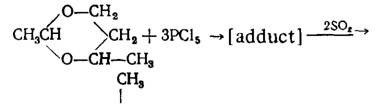
The properties of β-chloroethoxyvinyldichlorophosphonic acid agreed with data for the product synthesised by the reaction of β-chloroethyl vinyl ether with phosphorus pentachloride[49]. The characteristics of this reaction confirm its electrophilic mechanism. Electropositive substituents in the 2- and 4-positions facilitate the process appreciably and increase the yield of the final phosphonate[50]. An electron withdrawing substituent in the 4-position lowers the rate of the process and makes it possible to isolate the intermediate α-halogeno ether[51]:



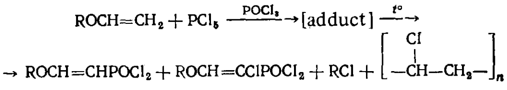
When the product is decomposed by hydrogen sulphide, derivatives of phosphonothioic acids are obtained. Thus the possibilities associated with these reactions can be described schematically as follows:



Derivatives of 1,3-dioxan containing an alkyl substituent in the 2-position react similarly with phosphorus pentachloride[52]:



In contrast to adducts with vinyl ethers, complexes with the above dioxolans and dioxans lead to the formation of phosphonates on heating[53]. This is caused by the phosphoryl chloride formed in the initial stages:

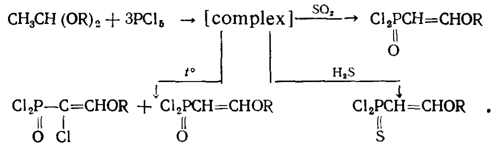


$$\mathrm{ROCH{=}CH_2 + PCl_5 \xrightarrow{POCl_3} [adduct] \xrightarrow{t^\circ}}$$

$$\mathrm{\rightarrow ROCH{=}CHPOCl_2 + ROCH{=}CClPOCl_2 + RCl + \left[\begin{matrix} Cl \\ | \\ -CH-CH_2- \end{matrix}\right]_n} .$$

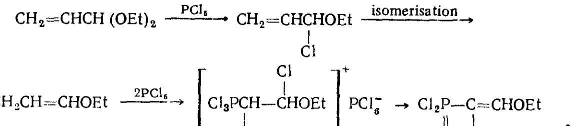
3. Phosphorylation of Acetals, Mercaptals, Hemiacetals, and Hemimercaptals

Oxa- and hydroxy-derivatives of hydrocarbons have been phosphorylated by phosphorus pentachloride[55]. The authors demonstrated the error of the earlier views[56] concerning the retention of the acetal group in the reaction and proposed the following mechanism for the phosphorylation of acetals:



They suggest that β-alkoxyvinylphosphonic dichloride and β-alkoxyvinylphosphonothioic dichloride are formed via an α-chloro-ether, as suggested previously[41]. The formation of β-alkoxy-α-chlorovinylphosphonic dichloride was explained by the occurrence of consecutive reactions: chlorination of the multiple bond of β-alkoxyvinylphosphonic dichloride and dehydrochlorination on heating during distillation. It was shown subsequently that ketals and acetals react with phosphorus pentachloride[57]. Bromoacetals do not enter into this reaction, most probably owing to the difficulty of the dehydrochlorination of the $\alpha\beta$-dihalogeno-ethers. Nor was it possible to isolate a phosphonate in the reaction with ethoxyacetal.

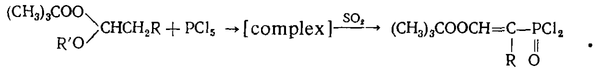
The reaction of acrolein acetals, which have two nucleophilic centres (the multiple bond and the acetal group) is interesting[58]. Studies on the structure of the final product, which is 1-chloro-3-ethoxyprop-2-enylphosphonic dichloride (the dichloride of 1-chloro methyl-2-ethoxyvinylphosphonic acid) suggested the following reaction mechanism:



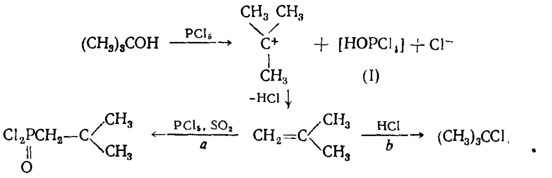
$$CH_2{=}CHCH(OEt)_2 \xrightarrow{PCl_5} CH_2{=}CH\underset{\substack{|\\ Cl}}{C}HOEt \xrightarrow{\text{isomerisation}} \rightarrow ClCH_2CH{=}CHOEt \xrightarrow{2PCl_5} \left[Cl_3P\underset{\substack{|\\ CH_2Cl}}{C}H-\overset{\substack{Cl\\ |}}{C}HOEt \right]^+ PCl_6^- \rightarrow Cl_2\underset{\substack{\|\\ O}}{P}-\underset{\substack{|\\ CH_2Cl}}{C}{=}CHOEt \;.$$

The reaction can be carried out with hemiacetals and hemimercaptals without their isolation and involves in essence the treatment with phosphorus pentachloride of mixtures of the alcohol (mercaptan) and aldehyde.[59] The yield of phosphonic dichlorides was, however, very low.

Phosphorus-containing unsaturated peroxides were obtained by the reaction of phosphorus pentachloride with acetals, acetates, and allyl ethers of α-hydroxyalkyl t-butyl peroxides[60]. It is of interest that the peroxy-group is preserved in this reaction:



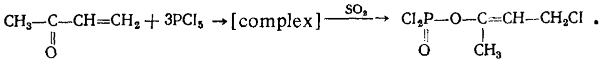
Many tertiary alcohols and their derivatives (ethers and esters) proved to be capable of being phosphorylated by phosphorus pentachloride under mild conditions[61,62]. The substitution of the hydroxy-group by chlorine proved to be a competing reaction under these conditions. It is suggested that in both cases the process begins with electrophilic attack by phosphorus pentachloride on the nucleophilic oxygen of the hydroxy- or ether group. This results in the formation of an olefin via a carbonium ion and complex (I). The decomposition of complex (I) into phosphoryl chloride and hydrogen chloride tends to increase the content of butyl chloride; a decrease of temperature lowers the rate of decomposition of the complex and promotes *C*-phosphorylation:



The phosphorylation of methyl phenyl ketone has been observed by Dogadina et al.[63], while Fokin et al.[64] showed that this possibility also exists for aliphatic ketones. It has been noted that 2-chloroalkenylphosphorus chlorides are formed in very small amounts. The reaction leads to the synthesis mainly of chloro-derivatives by the mechanism:

$$RC(O)CH_3 + PCl_5 \rightarrow RCCl_2CH_3 \xrightarrow{-HCl} RCCl{=}CH_2 \xrightarrow[-HCl]{+PCl_5} \rightarrow RCCl{=}CHPCl_4 \xrightarrow[-PCl_3]{} RCCl{=}CHCl \;.$$

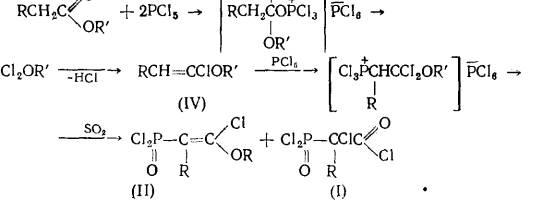
Methyl vinyl ketone reacted via the 1,4-addition mechanism, as in the phosphorylation of dienes[65]:



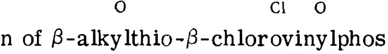
$$CH_3-\underset{\substack{\|\\ O}}{C}-CH{=}CH_2 + 3PCl_5 \rightarrow [\text{complex}] \xrightarrow{SO_2} Cl_2\underset{\substack{\|\\ O}}{P}-O-\underset{\substack{|\\ CH_3}}{C}{=}CH-CH_2Cl \;.$$

4. Phosphorylation of Esters

The reactions of phosphorus pentachloride with esters have been investigated in detail[66,67]. Analysis of the yields of products as a function of the reaction of the complex led the authors to the quite justified conclusion that the reaction proceeds via the addition of phosphorus pentachloride to the carbonyl group of the ester and that the adduct gradually decomposes to the $\alpha\alpha'$-dichloro-ether (III), which is dehydrochlorinated under the reaction conditions to the unsaturated α-chloro-ether (IV). This product undergoes further phosphorylation, similar to that of di-(α-chloroethyl) ether, by phosphorus pentachloride[68]:



Phosphorylation by phosphorus pentachloride is not restricted to the examples indicated above. It was found that dialkyl sulphides[69] also react with phosphorus pentachloride. The reaction has its characteristic features, because it gives rise to two types of phosphonic dichlorides as a function of temperature:



$$R-S-CH{=}CH\underset{\substack{\|\\ O}}{P}Cl_2 \quad \text{or} \quad R-S-\underset{\substack{|\\ Cl}}{C}{=}CH\underset{\substack{\|\\ O}}{P}Cl_2 \;.$$

The formation of β-alkylthio-β-chlorovinylphosphonic dichloride was noted for the first time[70].

The synthetic possibilities of the reactions with phosphorus pentachloride are very extensive and have been confirmed by the latest communications[71,72] concerning the reduction of phosphorus pentachloride–olefin adducts by reaction with silanes containing one or several Si–H bonds. The dichlorophosphines evolved under these conditions serve as the starting materials for the synthesis of a whole series of products.

The results of recent years examined above demonstrate the exceptional reactivity of phosphorus pentachloride and the wide scope of its use for the synthesis of phosphonates, which have found practical applications[73].

IV. THE MECHANISMS OF THE REACTIONS OF PHOSPHORUS PENTACHLORIDE

1. The Chlorination Reactions

Consideration of the chemical properties of phosphorus pentachloride suggests that it is an electrophile. This has been strikingly demonstrated by its reactions with alcohols, water, and organic acids. In relation to tertiary amines, phosphorus pentachloride exhibits the properties of a Lewis acid and yields salt-like adducts[74]. Acid properties are also shown in the reaction of phosphorus pentachloride with various derivatives of four-coordinated phosphorus containing the phosphoryl group and the reaction then involves the latter[75,76]:

$$PCl_5 + R_3P{=}O \rightarrow [Cl_5\bar{P}-O-\overset{+}{P}R_3] \;.$$

The five-coordinated derivatives of phosphorus are hard Lewis acids and form stable six-coordinated neutral complexes[77]. It is believed[78] that phosphorus pentachloride forms a negative ion even on reaction with hydrogen chloride:

$$PCl_5 + HCl \rightleftarrows H^+PCl_6^- \ .$$

The weakening of acid properties in the series of halides leads to a gradual substitution of the halogen by hydrocarbon groups[79,80]:

$$RPX_4 > R_2PX_3 > R_3PX_2; X = F, \text{or Cl}.$$

The pentahalides exhibit basic properties much more rarely. In these reactions they are converted into structures with a lower coordination [number]. Such processes include the above examples of reactions with aluminium chloride and iron(III) chloride. The following mechanism has been proposed in an interesting communication[75]:

$$F_3B \cdot NH_2CH_3 + 2PCl_5 \rightarrow CH_3N\begin{smallmatrix} \diagup \overset{+}{P}Cl_3 \\ \diagdown \overset{-}{B}Cl_3 \end{smallmatrix} + PF_3Cl_2 + 2HCl \ .$$

The lack of broad and specific studies on the reaction stages and of data on the structure of phosphorus pentachloride at the instant of the reaction precludes a unique representation of the mechanisms of reactions with its participation.

The mechanism of the interaction of phosphorus pentachloride with ketones has been deduced[81] on the hypothesis that it reacts in an ionic form and undergoes a series of successive transformations:

$$2PCl_5 \rightleftarrows \overset{+}{P}Cl_4\overset{-}{P}Cl_6 \ , \tag{1}$$

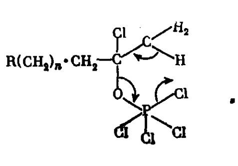
$$RCOCH_3 + \overset{+}{P}Cl_4 \leftrightarrows \left[\begin{array}{l} R\overset{+}{C}CH_3 \\ \ \ | \\ \ \ OPCl_4 \end{array}\right] , \tag{2}$$

$$\begin{array}{l} R\overset{+}{C}-CH_3 \\ | \\ OPCl_4 \end{array} + Cl^- \rightarrow \left[\begin{array}{c} Cl \\ | \\ R-C-CH_3 \\ | \\ OPCl_4 \end{array}\right] , \tag{3}$$

$$\begin{array}{l} \ \ Cl \\ \ \ | \\ RC-CH_3 \\ \ \ | \\ OPCl_4 \end{array} - \begin{cases} \xrightarrow{a} \begin{array}{l} \ \ Cl \\ \ \ | \\ RC{=}CH_2 + POCl_3 + HCl \end{array} \\ \xrightarrow{b} \begin{array}{l} \ \ Cl \\ \ \ | \\ R\underset{+}{C}-CH_3 + POCl_3 + Cl^- \end{array} \end{cases} , \tag{4}$$

$$\left[\begin{array}{c} Cl \\ | \\ R-\underset{+}{C}-CH_3 \end{array}\right] + Cl^- \rightarrow RCCl_2CH_3 \ . \tag{5}$$

The reaction begins with electrophilic attack on the carbonyl oxygen. The stage involving the formation of the chloro-olefin can, however, be represented, as in a later study[82], by a six-membered cyclic intermediate:



The different results obtained in the interaction of ketones with phosphorus pentachloride, using different solvents, were explained[83] by the different forms in which phosphorus pentachloride can exist: dimeric or monomeric. Depending on this factor, mechanisms were proposed for the reaction with benzylidenedeoxybenzoin. The influence of the solvent on the mechanism of the reaction with ketones was noted also in subsequent investigations.

Together with these mechanisms, the possible radical chlorination of benzene homologues[84] via the mechanism

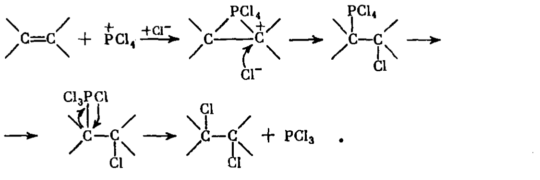
$$PCl_5 \rightleftarrows PCl_3 + Cl_2; \quad Cl_2 \rightleftarrows 2Cl^{\cdot}$$

or

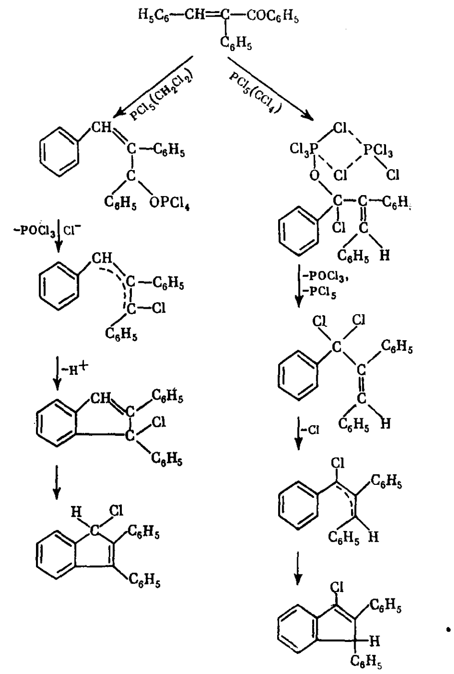
$$PCl_5 + R^{\cdot} \rightarrow RCl + {}^{\cdot}PCl_4; \ PCl_4 + RH \rightarrow R + HPCl_4; \ HPCl_4 \rightarrow PCl_3 + HCl$$

when a catalyst is present, has been reported.

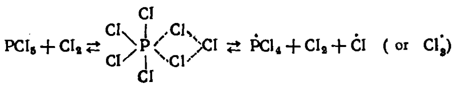
The following competing ionic mechanism has been put forward[84]:



The mechanism of the interaction of benzylidenedeoxybenzoin with phosphorus pentachloride in CCl_4 and CH_2Cl_2 is as follows:



It is believed[85] that catalysts of reactions involving chlorination by phosphorus pentachloride is due to its ability to be coordinated to a chlorine molecule, which favours the homolysis of the Cl–Cl bond:



Disregarding the numerous communications where the chlorinating activity of phosphorus pentachloride is reported[86], we shall examine the existing views on the mechanisms of its interaction with various types of hydrocarbons, which results in the formation of the phosphorus-carbon bond. Since studies on the phosphorylation by phosphorus pentachloride of compounds containing a multiple bond have already been described in other reviews[1,2], we shall examine below studies concerning the process mechanism.

2. The Phosphorylation Reactions

The most systematic studies, carried out by Bergman and Bondi[87], showed that the addition of phosphorus pentachloride occurs readily in reactions with asymmetrically substituted ethylene derivatives and leads to the formation of products whose hydrolysis gives rise to unsaturated phosphonic acids and the following mechanism was proposed:

$$RCH{=}CH_2 + PCl_5 \rightarrow RCHClCH_2PCl_4 \xrightarrow[-5HCl]{3H_2O} RCHCHP({=}O)(OH)_2\ .$$

The authors[87] did not isolate the intermediate, but noted that high yields require at least a twofold excess of phosphorus pentachloride.

Later studies[88,89] showed that the addition of phosphorus pentachloride to a multiple bond takes place in such a way that the $\overset{+}{P}Cl_4$ group adds to the most hydrogenated carbon atom, while the chlorine atom adds to the least hydrogenated carbon atom. The addition products can be regarded as binary compounds with phosphorus pentachloride:

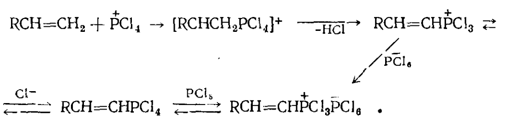
$$RCH{=}CH_2 + 2PCl_5 \rightarrow RCHClCH_2PCl_4 \cdot PCl_5\ .$$

It has been suggested[90] that the reaction of phosphorus pentachloride with unsaturated hydrocarbons may proceed without the formation of β-chlorophosphonic acid derivatives via an ionic mechanism:

$$RCH{=}CH_2 + {}^{+}PCl_4 \rightarrow R\overset{+}{C}HCH_2PCl_4 \xrightarrow[-HCl]{} RCH{=}CH\overset{+}{P}Cl_3 \xrightarrow{+{}^{-}PCl_6} RCH{=}CH\overset{+}{P}Cl_3PCl_6.$$

The formation of the intermediate addition product $ArCHClCH_2.PCl_4$ is believed to be unlikely[90]. In the reaction with styrene the structure $C_6H_5CH{=}CH\overset{+}{P}Cl_3\overset{-}{P}Cl_6$ is attributed to the complex, which takes into account its ability to interact with sulphur dioxide, styrene, and red phosphorus. These reactions are regarded as confirmation of the structure of the complex.

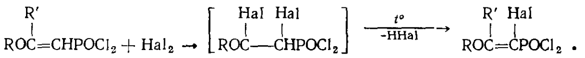
Grechkin and Kalabina[91] treat the above reaction as electrophilic substitution of hydrogen. They suggest that the reaction begins with the formation of a π-complex of the olefin and the $\overset{+}{P}Cl_4$ cation, which is stabilised after the elimination of hydrogen chloride. The resulting cation can react, according to the authors, with a Cl^- ion, whereby it is converted into alkenyltetrachlorophosphorane, or with a PCl_6^- ion, giving rise to a salt-like product. The mechanism is outwardly similar to that described by Fedorova and Kirsanov[90]:



$$RCH{=}CH_2 + \overset{+}{P}Cl_4 \rightarrow [RCHCH_2PCl_4]^+ \xrightarrow[-HCl]{} RCH{=}CH\overset{+}{P}Cl_3 \rightleftarrows$$
$$\xrightleftharpoons{Cl^-} RCH{=}CHPCl_4 \xrightleftharpoons{PCl_5} RCH{=}CH\overset{+}{P}Cl_3\overset{-}{P}Cl_6\ .$$

These mechanisms take into account the fact that, in the interaction with styrene or vinyl ethers[92], the addition of the phosphorus pentachloride-chlorine fragment to the multiple bond is not observed.

The authors concluded[90,91] that an electrophilic substitution mechanism operates solely on the grounds that no-one has isolated β-chloro-β-phenylethylphosphonate on phosphorylating styrene and that the reaction always leads to a compound with a multiple bond—styrylphosphonic dichloride (this also applies to the products of the interaction of phosphorus pentachloride with vinyl ethers). However, this cannot be regarded as proof of the mechanism, because the proton in the α-position relative to the phosphoryl group is known to be highly mobile, which was noted for the first time by Kabachnik[93,94]. As regards vinyl ethers, we may note the enhancement of the mobility of chlorine under the influence of the alkoxy-group. The elimination of hydrogen chloride from a series of α-halogeno-ethers is known to occur under very mild conditions[95]. In the intermediate phosphorylation products these substituents act in concert, leading to the formation of phosphonates containing a multiple bond. The halogenation of β-alkoxyvinylphosphonic dichlorides may serve as a model[96-98]:



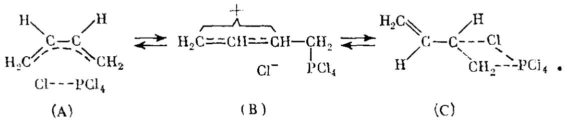
$$RO\overset{R'}{\overset{|}{C}}{=}CHPOCl_2 + Hal_2 \rightarrow \left[RO\overset{Hal}{\overset{|}{C}}{-}\overset{Hal}{\overset{|}{C}}HPOCl_2\right] \xrightarrow[-HHal]{t^\circ} RO\overset{R'}{\overset{|}{C}}{=}\overset{Hal}{\overset{|}{C}}POCl_2\ .$$

The phosphorylation of aliphatic olefins leads correspondingly to products without a multiple bond[99]:

$$RCH{=}CH_2 + PCl_5 \rightarrow [\text{adduct}] \xrightarrow[-SOCl_2]{SO_2} RCHClCH_2POCl_2$$
$$RCH{=}CHPOCl_2 + Br_2 \rightarrow RCHBrCHBrPOCl_2\ .$$

In a series of studies[100,102] on the phosphorylation of diene and acetylene derivatives by phosphorus pentachloride carried out in recent years a molecular reaction mechanism is postulated. It is believed that, in the reaction of phosphorus pentachloride with unsaturated hydrocarbons, several mechanisms may operate, differing in the degree of charge separation in the transition state and in the lifetime of the polarised structure, which leads, depending on the initial hydrocarbons, to the formation of products whose structure is determined by the process kinetics (acetylenes) or thermodynamics (dienes).

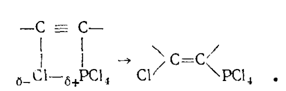
On the grounds of stereochemical considerations, the transition state in the reaction with dienes is believed to be highly polar and to incorporate the covalent structures A and C and structure B with separated charges:



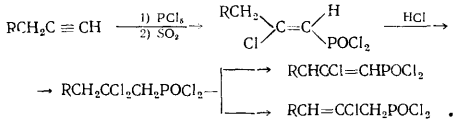
In the case of dienes the transition state is closer to the polarised structure B and this is sufficient for the occurrence of a rearrangement and the formation of thermodynamically more favourable isomers.

The stereospecific *cis*-addition to an isolated triple or double bond is believed[103] to be a confirmation of the addition of the phosphorus pentachloride molecule in a pentacovalent form.

The nature of the influence of substituents at the multiple bond on the mode of addition of the phosphorus fragment shows unambiguously that the addition process has an electrophilic mechanism and probably proceeds via a four-membered cyclic transition state:



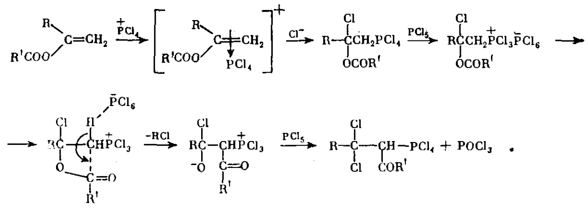
The possibility of a prototropic rearrangement in the reaction with acetylenic derivatives, leading to 2-chloroalk-2-enylphosphonic acids, has been examined[104]: however, other workers[105] reject the possibility of isomerisation, particularly since a prototropic rearrangement takes place in the presence of bases[106]. Bearing this in mind, Meisters and Swan[104] believe that the alk-2-enyl isomer is formed as a result of the addition-elimination of a further hydrogen chloride molecule:



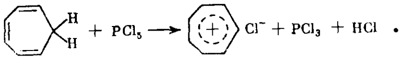
The results of the latest studies by Rybkina et al.[107] support a molecular mechanism of addition to multiple bonds. In their studies on the phosphorylation of olefins in different aprotic solvents the authors showed that in polar solvents, promoting the existence of phosphorus pentachloride in the form of an ionic dimer, the yields of the reaction products are a minimum, while in non-polar solvents, where phosphorus pentachloride exists in a molecular form, they are a maximum.

Finally, in connection with the discussion of the mechanisms of the phosphorylation reactions of ethers, acetals and cyclic oxa- and dioxa-compounds, we shall consider briefly studies where the dehydrogenating activity of phosphorus pentachloride was noted. This pathway was observed for the first time in the reaction of α-benzylstilbene with phosphorus pentachloride, which resulted in ring closure and the formation of 2,3-diphenylindene.[87,107]

In a study of the phosphorylation of esters containing a multiple bond by phosphorus pentachloride, Lutsenko and coworkers[109-114] included a deprotonation stage in the process mechanism:



Phosphorus pentachloride behaves similarly in the reaction with cycloheptatriene, which results in the formation of tropylium chloride, phosphorus pentachloride being reduced to the trichloride[115]:



In conclusion we shall consider the role of the formation of a complex by phosphorus pentachloride with an electrophile and nucleophilic centres: oxygen or a multiple bond. The transformations of the adducts of phosphorus pentachloride with vinyl ethers[54], styrene derivatives, and α-alkoxystyrene[116,117] may be regarded as an indirect confirmation of the formation of molecular donor–acceptor complexes by phosphorus pentachloride:

$$C_6H_5CH{=}CH_2 + PCl_5 \xrightarrow{t^\circ} C_6H_5CH{=}CClPCl_2 + 2HCl \;;$$

$$C_6H_5C(OR){=}CH_2 + PCl_5 \xrightarrow{t^\circ} C_6H_5CCl{=}CH_2 + POCl_3 \;;$$

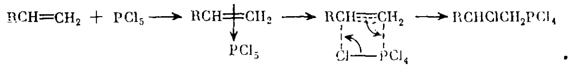
$$ROCH{=}CH_2 + PCl_5 \rightarrow [\text{adduct}] \xrightarrow{t^\circ} \text{chlorinated products};$$

$$2ROCH{=}CH_2 + PCl_5 \xrightarrow{POCl_3} [\text{adduct}] \xrightarrow{t^\circ}$$

$$\rightarrow ROCH{=}CHPOCl_2 + POCl_3 + RCl + [\overset{|}{C}H{-}CH_2{-}]_n + HCl \;.$$

Phosphorus-containing substances are formed only in those cases where it is possible to postulate the coordination of phosphorus pentachloride to a multiple bond (styrene). α-Alkoxystyrene and vinyl ethers react with phosphorus pentachloride to form only chlorination products, possibly owing to the formation of a complex involving the coordination of the alkoxy-group to an oxygen atom. The introduction of phosphoryl chloride into the reaction mixture in the process involving vinyl ethers promotes the formation of phosphorus-containing vinyl ethers.

The data examined suggest that the interaction of phosphorus pentachloride with olefins involves the following probable stages: (a) the formation of a donor–acceptor complex; (b) electrophilic addition of fragments of phosphorus pentachloride (Cl and PCl_4) to the double bond:



$$RCH{=}CH_2 + PCl_5 \rightarrow \underset{PCl_5}{RCH{=}CH_2} \rightarrow \underset{Cl{-}PCl_4}{RCH{=}CH_2} \rightarrow RCHClCH_2PCl_4 \;.$$

During the preparation of the review for the press, new original reports were published. Studies on keten[118] showed that phosphorus pentachloride interacts with it to form a phosphorus–carbon bond. The possibility of the simultaneous formation of bonds with two carbon atoms has been illustrated[119] in relation to the reaction with bis(α-chloromethylvinyl) sulphide.

In conclusion we may note that the preparative possibilities of phosphorus pentachloride in the syntheses of compounds with a phosphorus–carbon bond continue to expand. Among carbon-containing compounds, studies are being made not only on compounds with a multiple bond but also on those which are capable of forming multiple bonds under the influence of phosphorus pentachloride. It would be premature to express any definite view concerning the mechanism. The reactions with phosphorus pentachloride are complex and probably have a whole range of different mechanisms. It appears essential to investigate in greater detail the individual stages of the reactions, in the first place complex formation, and to elucidate the role of the third agent—sulphur dioxide, hydrogen sulphide, etc.

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Heterogeneous Metal Complex Catalysts

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The review is devoted to methods of synthesis and catalytic properties of heterogeneous metal complex catalysts in which the selectivity and activity of homogeneous metal complexes and the technological advantages of traditional heterogeneous catalysts are combined. The adsorption and chemical interactions between the transition metal complexes and solid carriers (organic and mineral) are discussed and the activities and selectivities of heterogeneous metal complex catalysts and their homogeneous analogues are compared. Studies published up to 1976 are considered.
The bibliography includes 203 references.

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I. INTRODUCTION

We are witnessing a vigorous growth of research in the field of homogeneous metal complex catalysis. Catalysis by transition metal complexes (TMC) is finding an increasing number of new applications as regards both theoretical and applied aspects: oxidation of hydrocarbons, stereospecific polymerisation, homogeneous hydrogenation, hydroformylation, and fixation of molecular nitrogen. This is by no means a complete list of the fields in which metal complex catalysts are used. However, although they have definite advantages over the traditional heterogeneous catalysts (high overall activity and selectivity), homogeneous catalysts suffer from significant disadvantages: their application requires the introduction into the process of a stage in which the reaction products and the catalyst are separated. The difficulty of isolating the catalyst from the reaction mixture and the difficulties associated with its reuse are responsible for the relatively small contribution of homogeneous catalytic processes to industry. The only exception is the polymerisation process in which the catalyst remains incorporated in the high-molecular-weight compound, which, incidentally, has an undesirable influence on the quality of the latter.

There is no doubt that in the foreseeable future heterogeneous catalysis will become dominant in industrial processes. Consequently catalytic systems involving heterogeneous catalysts based on transition metal complexes will be vigorously developed. Catalysts of this kind have come to be referred to as "hybrid"; it is believed that they are capable of ensuring the high selectivity and activity characteristic of homogeneous metal complexes and the technological usefulness characteristic of traditional heterogeneous catalysts. The development of studies in this field is hindered by the inadequacy of the theoretical ideas concerning the nature of the action of hybrid catalysts. For example, the problems of the influence of ligands on the catalytic activity of the metal ion, of the dependence of the catalytic activity on the carrier structure and on the number of transition metal atoms in the active centre, and the possibility of the occurrence of reaction on metal complexes in the absence of a solvent, etc. remain unsolved. A number of reviews have been devoted[1-16] to the synthesis and properties of heterogeneous catalysts obtained as a result of the conversion of transition metal complexes into heterogeneous formations on mineral and polymeric carriers.

Commereuc and Martino[13] suggest that heterogeneous catalytic systems be classified on the basis of three features: (1) the type of initial compound containing the transition metal atom; (2) the method used to activate the heterogeneous system; (3) the nature of the carrier-matrix. Although such classification is undoubtedly useful, it does not provide any information about the nature of the bond between the TMC and the carrier, which is very important from the standpoint of both the stability of the hybrid catalyst obtained and the interpretation of the results. Heterogeneous metal complex catalysts can be divided into the following types in terms of the nature of the bonds between the TMC and the carrier: (1) adsorption fixation of the TMC on the carrier; (2) binding of the TMC by ion-exchange resins; (3) π-coordination of the TMC on the carrier, which plays the role of a macroligand; (4) σ-binding of the TMC by the functional groups of the carrier; (5) the incorporation of the TMC in polymer gels.

It is readily seen that the methods used to convert the TMC into heterogeneous systems have much in common with those for the immobilisation of enzymes[17]. The main difficulty arising in the formation of heterogeneous systems from TMC is that the catalytic activity of the complex is caused either by the presence of a weakly bound ligand in the coordination sphere or the presence of a free coordination site. The interaction of the TMC with the carrier usually occurs via this "weak unit", which inevitably entails a loss of catalytic activity.

We shall consider below various methods for the conversion of the TMC into heterogeneous systems, noting, incidentally, the nature of the catalytic activity and, wherever possible, comparing the hybrid catalysts with their homogeneous analogues.

II. ADSORPTION BINDING OF TRANSITION METAL COMPLEXES

The first studies on the conversion of TMC into heterogeneous systems were concerned with the physical adsorption of such complexes on mineral carriers[18-23]. The general principle underlying the preparation of catalytic systems of this kind may be considered in relation to the study of Acres et al.[18] The familiar homogeneous isomerisation catalyst[24-26] $RhCl_3.3H_2O$ was dissolved in ethylene glycol and the resulting solution was added to a suspension of silica gel in methanol; after the removal of methanol, the catalyst showed a high activity in the isomerisation of pent-1-ene. Using the same method, Rony[21,27] compared the $(PPh_3)_2Rh(CO)Cl/SiO_2$ catalyst, which propagates the hydroformylation of propene. A similar catalytic system was prepared by Bond[28], who deposited the complex $RhH(CO)(PPh_3)_3$ on silica gel.

The study of the influence of the conditions of the catalytic process on the properties of the catalyst showed that four complexes converted into heterogeneous systems on a mineral carrier [$RhCl_3$ in the isomerisation reaction and $(PPh_3)_2Rh(CO)Cl$, $(AsPh_3)_2Rh(CO)Cl$, and $Co_2(CO)_6(PBu_3)_2$ in the hydroformylation reaction] are more active in the liquid-phase process, while Wilkinson's catalyst $(PR_3)_3.$ $.PhCl$ is more active under the conditions of a gas-phase process[29].

TMC have been deposited on mineral carriers also by controlled adsorption from the gas phase. Vasserberg and coworkers[30] prepared a nickel–alumina catalyst by the adsorption of nickel tetracarbonyl on alumina at a reduced pressure. After reduction with hydrogen (at 400° C for 12 h), the activity of the specimen was investigated in the reduction of carbon dioxide to methane and proved to be higher than that of specimens with the same amount of metal but obtained by precipitation or by impregnation of silica gel with nickel salts. This result can probably be accounted for by the significantly higher degree of dispersion of the metallic nickel obtained from the carbonyl.

A catalyst for the disproportionation of propene,

$$2C_3H_6 \rightarrow C_4H_8 + C_2H_4$$

has been obtained[31] from molybdenum hexacarbonyl. The authors found that the degree of reaction is highest in the range 290–340° and were also able to show that the active centre is the complex $Mo(CO)_x(C_3H_6)_{6-x}$ $(x = 3, 4)$.

The catalysts obtained by the deposition of $Mo(CO)_6$ on oxide carriers have also been studied[32-34]. Later investigations yielded more precise data on the nature of the active centres of deposited catalysts based on molybdenum hexacarbonyl[35,36] and the influence of poisons on their activity[37]. It is noteworthy that, when transition metal carbonyl compounds are adsorbed on oxide carriers, physical adsorption does not occur in all cases. Parkyns' study[38] of the interaction of nickel carbonyl with silica gel and alumina showed that, whereas the usual physical adsorption is observed on the former carrier, on the latter the vibration frequencies of the CO group in the infrared spectrum correspond to the vibrations of carbon monoxide adsorbed on nickel.

A number of studies have been made recently on the conversion of carbonyl cluster complexes into heterogeneous systems on mineral carriers[39-42]. The most interesting study[42] is that undertaken to compare the catalytic activities of the complexes Cp_2Ni, $Cp_2Ni_2(CO)_2$, and $Cp_3Ni_3(CO)_2$ ($Cp = \pi\text{-}C_5H_5$) "heterogenised" on silica gel. The nickel catalysts obtained by the decomposition of adsorbed complexes *in vacuo* at 80–120° C showed significant differences in their catalytic properties. Thus the catalyst obtained by the decomposition of nickelocene adsorbed on silica gel is active in the trimerisation of acetylene to benzene, unlike cluster systems. On the other hand, the H_2–D_2 exchange reaction and the hydrogenation of ethylene and benzene take place much more readily in the presence of polynuclear catalysts, while the hydroformylation reaction occurring in the presence of cluster catalysts does not take place at all in the presence of specimens obtained by the decomposition of adsorbed nickelocene.

The use of cluster compounds in catalysis opens new pathways in the formation of highly selective catalysts as well as catalysts capable of propagating structurally hindered processes[41,42]. From the standpoint of the theory of catalysis, a detailed study of such systems will make it possible to determine the structures of the active centres of traditional catalysts in various processes.

Catalysts based on cobalt, copper, silver, and platinum have been obtained by impregnating mineral carriers with TMC solutions[43-45]. A study of the low-temperature conversion of carbon monoxide over the CuO/SiO_2 and CuO/Al_2O_3 catalysts established that[43] specimens obtained from the amminecopper complex exhibit a higher activity than those obtained by impregnating alumina and silica gels with copper nitrate. Comparison of the catalytic activities[46] of the $RhCl_3.3H_2O$/C(act.) and Rh_2O_3/C(act.) systems[47] in the carbonylation of methanol

$$CH_3OH + CO \xrightarrow[CHI_3(\text{ind.})]{} CH_3COOH$$

yielded a similar result[46]. By studying the kinetics of this reaction in the presence of the $RhCl_3.3H_2O$/C(act.) catalyst and by comparing them with those of the homogeneous catalytic carbonylation of methanol in the presence of the free rhodium complex, the authors[46] found that the process mechanisms are the same in the two instances.

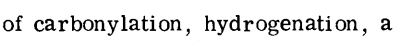
An interesting method of synthesis of hybrid adsorption catalysts was proposed by Mochido et al.[48] Using the Cu(II)–Y zeolite, obtained by ion exchange in an ammonia solution, as the carrier, they treated it in one case with ethylenediamine (EDA) and in another with dimethylglyoxime (DMG). The study of the infrared spectra showed that copper chelate complexes are formed with the organic reagents; the systems can be represented as Cu–DMG/Cu–Y and Cu–EDA/Cu–Y. The authors[48] studied the catalytic properties of the specimens in the decomposition of hydrogen peroxide and established that one complex molecule on the surface decomposes approximately 400 H_2O_2 molecules. It was observed that the activity of the Cu–EDA/Cu–Y catalyst is five times higher than the activity of the zeolite untreated with EDA; on the other hand, the Cu–DMG/Cu–Y specimen exhibits a lower activity than the initial zeolite.

A comparative study of the dimerisation of propene in the presence of homogeneous and heterogeneous catalytic systems incorporating nickel acetylacetonate and an organoaluminium compound has been carried out[49,50]. The authors were able to show that the adsorption of the catalyst on porous mineral carriers with a high specific surface leads not only to an increase of the stability of the action of the catalysts, but also to an increase of their thermal stability.

In conclusion of this Section one should note that a common deficiency of the adsorption methods for the conversion of TMC into heterogeneous systems is the low strength of the bond between the physically adsorbed complex and the carrier, which leads to the elution of the TMC from the carrier surface during the reaction. Furthermore, physical adsorption may entail the formation of polymolecular TMC layers, which lowers the efficiency of the active compound and may cause agglomeration of the complex, which also reduces the efficiency.

III. THE BINDING OF TRANSITION METAL COMPLEXES BY ION-EXCHANGE RESINS

The interaction of a cation-exchange resin with acid sodium tungstate led to the synthesis of a catalyst for the oxidation of maleic acid[51,52]:



A number of carbonylation, hydrogenation, and hydroformylation catalysts, obtained by the conversion of Group VIII transition metal complexes into heterogeneous systems on ion-exchange resins, have been patented[53-60]. Thus a method has been described[55] for the preparation of catalysts based on $[Pd(NH_3)_4]^{2+}$ with low- and high-molecular-weight counterions; the former catalysed the interaction of allyl chloride with carbon monoxide in a homogeneous system and the latter catalysed the same reaction in a heterogeneous system:

$$CH_2{=}CH{-}CH_2Cl + CO \rightarrow CH_2{=}CH{-}CH_2COCl\ .$$

It was found that both catalysts exhibit comparable activities and selectivities in the above reaction.

Hanson and coworkers[61,62] prepared hybrid catalysts using a sulphonated styrene–divinylbenzene copolymer containing sodium phosphinate groups as the ion exchanger. They investigated the reduction of the catalysts by hydrogen and hydrazine after the interaction of the ion exchangers with ammine complexes of platinum, palladium, nickel, and silver and the catalytic activities of the resulting catalysts in the oxidation of ethanol. A similar study has been made[63-66] using hydroxylated Amberlite A-27 as the carrier. The $PdCl_4^{2-}$/A-27, $RhCl_6^{3-}$/A-27, and $Pd(PPh_3)_4^{2+}$/A-27 catalysts, which are active in the hydrogenation of unsaturated compounds, were obtained.

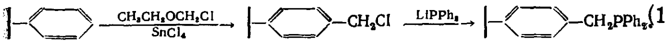
Berenblyum and coworkers[67-70] obtained an effective hybrid catalyst for the hydrogenation of olefins on the basis of a new water-soluble complex $NaH_3[(acac)Rh(O_2)_2.$ $.Rh(OH)(H_2O)]$, by converting it into a heterogeneous system on an ion-exchange resin containing amino-groups.

Hybrid catalysts obtained by converting metal complex ions into heterogeneous systems on ion exchangers have an important advantage over physically adsorbed TMC, which consists in a greater binding strength. A disadvantage of these heterogeneous hybrid catalysts is the impossibility of using them to prepare uncharged complexes, particularly zero-valent complexes, which are widely used.

IV. π-COORDINATION OF TRANSITION METAL COMPLEXES TO POLYMERIC PHOSPHINO-MACROLIGANDS

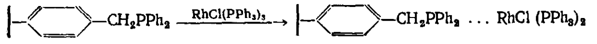
Manassen[5] suggested that the catalytic activities of free TMC and TMC bound to a polymer chain should exhibit differences due to the orientation of the polymeric ligand, steric hindrance, and the change in the stability constant of the complex. According to Patchornik and Kraus[71], the bond between a TMC and a stereoregular insoluble polymer restricts the motion of the active centre on the surface; if the distance between the active centres is sufficiently large, it is possible to achieve a dilution such that they do not interact with one another. The rate of reaction should be higher in this case than in the usual homogeneous catalysis, because, according to the authors[71], catalyst molecules in solution lose part of their energy as a result of mutual collisions. Having adopted this view, one must suppose that fixation on the carrier promotes an increase of the activity of homogeneous catalysts. However, as will be shown below, this is by no means always the case.

The most frequently used polymeric carrier for conversion into heterogeneous systems by coordination is the styrene–divinylbenzene copolymer containing the diphenylphosphine group. This carrier-macroligand is synthesised as follows[72-76]:



(1)

The presence of phosphino-groups in the polymer makes it possible to coordinate the TMC to the phosphorus atom. Thus a number of workers[73,77-81] converted the familiar homogeneous Wilkinson's catalyst[82] into a heterogeneous system on a phosphinated styrene–divinylbenzene copolymer, having replaced one of the triphenylphosphine ligands in each molecule of the complex by the polymer-diphenylphosphino-group of the carrier:

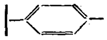


Their method involves the establishment of equilibrium between the TMC converted into the heterogeneous system and the TMC in the inert solvent from which the complex is deposited; at room temperature such equilibrium is established in 2–4 weeks[73].

The study of the catalytic activity of the catalyst thus prepared in the hydrogenation of olefins demonstrated a significant dependence of the reaction rate on the size of the substrate molecules. While the relative rates of hydrogenation *w* of hex-1-ene, 2-cholestene, octadecene, cyclo-octene, and cyclododecene on the homogeneous Wilkinson's catalyst are comparable, when the hybrid catalyst is used, they (*w*′) differ strongly:

Olefin	Cyclohexene	Hex-1-ene	Δ^2-Cholestene	Octadecene	Cyclo-octene.	Cyclododecene
w′	1.00	2.55	0.03	0.50	0.40	0.23
w	1.00	1.40	0.71	0.71	1.00	0.67

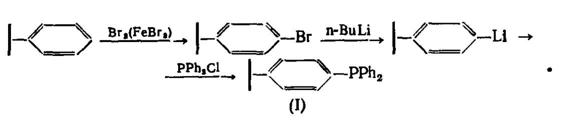
Thus it follows from the above investigation[73] that the conversion of a homogeneous catalyst into a heterogeneous system makes it possible to increase significantly its selectivity while retaining its high overall activity.

Analogous catalytic systems based on the styrene–divinylbenzene copolymer and different phosphine and chloride complexes of rhodium have been investigated[83,84]. The authors studied the possibility of using hybrid catalysts in hydroformylation and hydrosilylation reactions in addition to hydrogenation. By varying the low-molecular-weight ligands at the rhodium atom, the authors were able to choose catalysts for the selective hydrogenation of hept-1-ene, having almost completely excluded the parallel reaction involving the migration of the double bond. The catalyst —  $CH_2PPh_2...RhCl_x$ proved to be highly active in the hydrogenation reaction. An analogous catalyst had been obtained somewhat earlier[55].

Active hydroformylation catalysts were prepared by the above procedure from dicarbonylrhodium acetylacetonate and cobalt carbonyl[85,86]. The study of their catalytic activity in the hydroformylation of olefins[85] showed that they ensure 99% selectivity of conversion into an aldehyde for an overall degree of reaction of 87%.

Using Haag and Whitehurst's method[53], Bruner and Bailar[87,88] prepared a carrier based on the chloromethylated Amberlite HAD-4, containing benzyldiphenylphosphino-groups on the surface. Palladium and platinum chloride complexes were then coordinated to the phosphorus atom. The resulting catalysts were investigated in the hydrogenation of polyunsaturated hydrocarbons, and it was established that, for example, the palladium–polymer catalyst is extremely active in the selective hydrogenation of such hydrocarbons to mono-olefins. In addition, it has been found[87] that the hydrogenation of conjugated diene hydrocarbons proceeds faster than that of non-conjugated compounds. The platinum–polymer catalyst exhibits an activity under more severe conditions and its use requires the obligatory presence of tin chloride in proportions of Pt : Sn = 1 : 10.

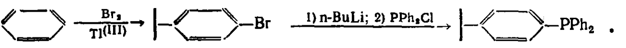
Yet another method of synthesis of the polymer matrix has been proposed by Collman and coworkers[89]:



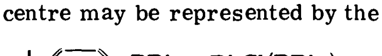
(I) (2)

An advantage of this method is the possibility of grafting the diphenylphosphino-groups directly to the benzene rings of the styrene–divinylbenzene polymer. The reaction of compound (I) with $Rh_4(CO)_{12}$ and $Rh_6(CO)_{16}$ yields polynuclear heterogeneous metal-complex catalysts. Collman et al.[89] showed that hybrid catalysts having the general formula $MClL_3$ (where M = Rh or Ir and L = I) are more active than their homogeneous analogues.

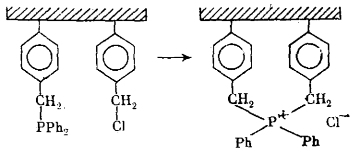
The above method has been modified[90] by brominating the benzene rings of the polymer in the presence of thallium(III) ions:



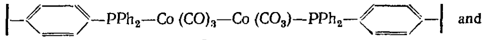
The authors[90] then coordinated Wilkinson's catalyst and obtained a hybrid hydrogenation catalyst. The degree of binding of the complex to the polymer in the above study[90] was 0.53 mmole g^{-1}, which is somewhat less than in the study of Collman et al.[89] The composition of the active centre may be represented by the formula

 By comparing the activities of the hybrid catalyst with Wilkinson's catalyst, the authors[90,91] established the following characteristics of the hydrogenation of olefins: (1) olefins with a terminal double bond are hydrogenated faster than those containing a double bond within a carbon chain; (2) *cis*-olefins are hydrogenated faster than the *trans*-isomers; (3) olefins are hydrogenated faster than acetylenes. The dependence of the rate of hydrogenation of two double bonds in conjugated cyclic dienes on the ring size (cyclo-octa-1,3-diene > cyclohexa-1,3-diene) was demonstrated, that for the hybrid catalyst being significantly more pronounced than for the homogeneous catalyst. The authors[90] also studied the appreciable difference between the ratio of the *cis*- and *trans*-isomers of *p*-menthanes obtained by the hydrogenation of 1,(7)-*p*-menth-1(7)-ene. Thus the ratio is 2.0 : 1 for tris-triphenylphosphinerhodium chloride, while for the hybrid catalyst it amounts to 3.1 : 1, i.e, in this case the use of the hybrid catalyst entails a shift towards a higher selectivity.

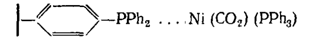
A hybrid catalyst based on the phosphinerhodium complex fixed on a polystyrene macroligand has been synthesised by Mitchell and Whitehurst[92]. The catalyst was found to have a low activity in the hydroformylation reaction, which the authors explain by the presence on the polymer surface of a quaternary phosphorus atom which is incapable of coordinating the transition metal:



The activities of hybrid and homogeneous catalysts have also been compared in studies[7,93] where cobalt and nickel complexes grafted to the styrene–divinylbenzene copolymer were synthesised and investigated:

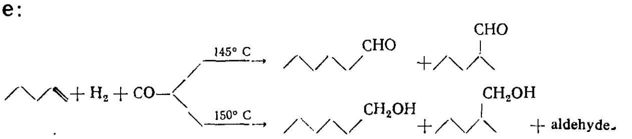


(II)



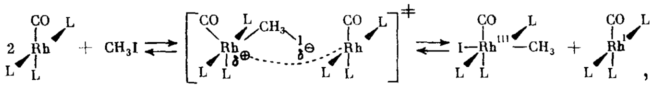
(III)

The former proved to be active in the isomerisation and hydroformylation reactions and the latter proved to be active in the cyclo-oligomerisation reaction. It is noteworthy that at high pressures the selectivity of the hydroformylation reaction is effectively regulated by temperature:



The hydroformylation of pent-1-ene has been studied[94] in the presence of the TMC $RhCl(CO)(PPh_3)_2$ and $RhH(CO).(PPh_3)_3$, converted into heterogeneous systems on a styrene–divinylbenzene matrix containing surface phosphino-groups. It was found that the catalytic activity and selectivity of the hybrid catalysts are the same as those observed for their homogeneous analogues.

In the general case the mechanisms of the action of the homogeneous and the corresponding hybrid catalysts are presumably the same, since the natures of their active centres are the same. However, it has been shown in relation to the carbonylation of methanol in the presence of the $RhCl(CO)(PPh_3)_2$ complex bound to a polymer[95] that the mechanisms of the homogeneous and heterogeneous catalytic reactions may differ. The difference was manifested by the change of the first order of the reaction with respect to rhodium to the second (for the hybrid catalyst), while the reaction was of zero order with respect to methanol and carbon monoxide and of first order with respect to methyl iodide (playing the role of a promoting agent) in reactions of both types. In view of their results, the authors[95] suggested that two rhodium centres are involved in the rate-limiting stage of the reaction in contrast to the mechanism of the homogeneous catalytic reaction:

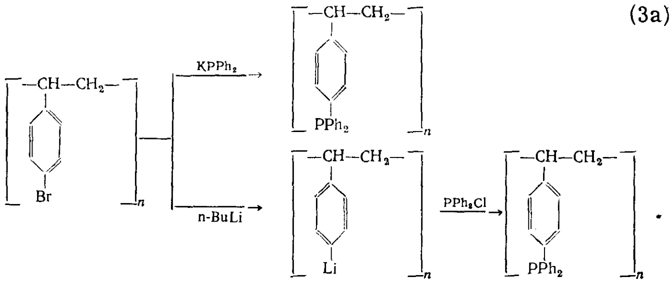


where L are polymeric and low-molecular-weight ligands which were not detected in the active form of the complex. According to this mechanism, the carbon of the CH_3I group undergoes nucleophilic attack by Rh(I) in the complex acting as a Lewis base; the second Rh(I) centre acts as a

Lewis acid, stabilising the transition state. This mechanism explains (although not completely) the possibility of the stereochemical formation of a transition state of this kind.

A large series of studies on the conversion of TMC into heterogeneous systems on polymeric carrier-macroligands containing phenylphosphino-groups have been carried out by Allum and coworkers[96-100], who showed[96] that, depending on the method of synthesis of the polymeric macroligand, it is possible to vary within wide limits the number of phosphino-groups fixed on the polymer. Thus, after treatment with potassium phenylphosphide, the polymer obtained by polymerising *p*-bromostyrene in the presence of benzoyl hydroperoxide contains 3.4 wt.% of phosphorus. A polymer containing 6 wt.% of phosphorus is obtained on synthesis via mechanism (3b), analogous to that proposed by Collman et al.[89] [see reaction (2) above]:

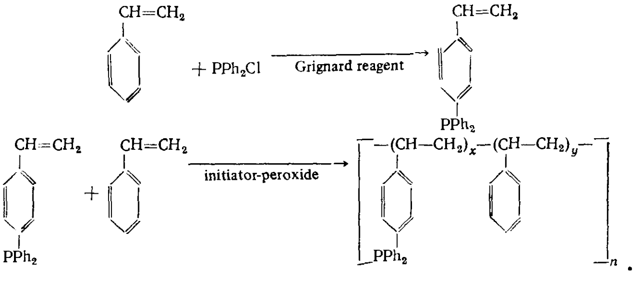
(3a)



(3b)

A somewhat smaller number of surface phosphino-groups is obtained in the synthesis of the matrix via reaction (1). In this case the polymer contains 4–5 wt.% of phosphorus.

A polymeric polystyrene matrix containing phosphino-groups can be obtained[5,93] by the polymerisation of *p*-diphenylphosphinostyrene[5,93]:



The preparation of other polymeric carrier-macroligands, suitable for the synthesis of hybrid catalysts and containing phosphino-groups, has been described[96-100]; poly(vinyl chloride), polychloroprene, polybutadiene, poly(vinyl alcohol), and other polymers have been used. Phosphino-groups were introduced into the first two polymers by direct reaction with $KPPh_2$. The phosphorus contents were respectively 11 and 3 wt.%. After preliminary treatment with hydrogen bromide, polybutadiene was treated with potassium diphenylphosphide, which yielded a product containing 6–8 wt.% of phosphorus. A phosphinated polybutadiene can also be obtained by the interaction of the initial polymer with diphenylphosphine under the influence of ultraviolet light[98]. Chlorodiphenylphosphine and dichlorophenylphosphine were used as phosphinating agents in the study with poly(vinyl alcohol). In the first case the polymer contained 1.7 and in the second 6–7 wt.% of phosphorus[96]. The authors suggest that the bond between phosphorus and carbon is formed via oxygen. The ready hydrolysability of this bond limited the practical application of the carrier. Nevertheless the above matrix makes it possible to employ phosphite groups in the conversion of TMC into heterogeneous systems.

Table 1. The composition of heterogeneous transition metal complexes.

Initial polymer	Polymeric ligand *P*, wt.%	TMC for conversion into heterogeneous form	
		TMC	metal, wt.%
Poly-*p*-bromostyrene	5.9	$CoCl_2$	0.7
Non cross-linked polystyrene	4.7	$CoCl_2$	4.3
Cross-linked polystyrene	4.35	$CoCl_2$	2.8
Amerlite HAD-2	2.0	$Ni(C_8H_{12})_2$	0.3
Amberlite HAD-2	2.0	$Rh(acac)\ (CO)_2$	2.0
Amberlite HAD-2	2.2	$[RhCl(C_8H_{12})]_2$	2.7
Poly-(vinyl chloride)	4.3	$CoCl_2$	4.6
Poly-(vinyl chloride)	4,75	$Rh(acac)\ (CO)_2$	7,3
Polybutadiene	7,9	$CoCl_2$	3.1

Table 1 presents the compositions of a series of heterogeneous TPM obtained by Allum et al.[96] It is noteworthy that complete information about the catalytic activity is available only for the TMC made heterogeneous on Amberlite, because only such hybrid catalysts are completely insoluble in the reaction media. It was found that the proportions of the phosphino-groups of the macroligand and the heterogeneous TMC may influence significantly the rate of the catalytic process. Thus the catalytic activity of a fixed iridium complex has been compared[101] with that of the analogous homogeneous catalyst in the hydrogenation of cyclo-octa-1,5-diene (1,5-COD) and the result shows that for P : Ir = 1 : 1 the degree of conversion of 1,5-COD in the presence of the polymer-bound catalyst is greater than for P : Ir < 5 (Table 2). The lower rate of the heterogeneous reaction compared with the homogeneous process for large P : Ir ratios was explained[101] by the low mobility of the heterogeneous complex.

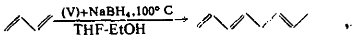
The influence of temperature on the catalytic activity of the hybrid catalyst was also noted[101]. The ratio of the activities at 170° and 80°C changed from 0.8 to 5 over the entire range of phosphorus contents in the polymer (from 1.91 to 10.28 wt.%). For a homogeneous catalyst, the ratio is always greater and lies in the range 8–10. Assuming the same mechanism of the catalytic activity over the entire temperature range, the authors explain this effect by the high mobility of the diphenylphosphino-groups fixed on the polymer.

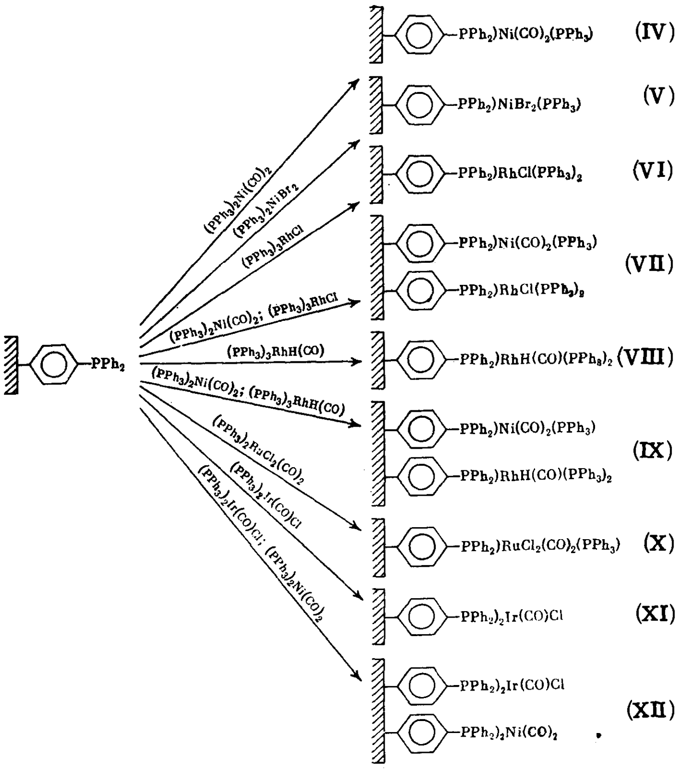
Thus it becomes evident that, in the study of the properties of hybrid catalysts containing a carrier-macroligand and when they are compared with homogeneous analogues, it is necessary to take into account factors such as the concentration and mobility of the surface-active groups responsible for the coordination of the TMC. This creates additional difficulties in comparing hybrid and homogeneous catalysts and in simulating catalysts with specified properties.

The studies of Pittman and coworkers[102,105] on the preparation of hybrid catalysts which propagate a sequential multistep catalytic process are of considerable interest. The idea of devising such catalysts was put forward by Mossbach[106], who immobilised simultaneously hexokinase and glucose-6-phosphate isomerase on polystyrene and achieved the sequential conversion of glucose, initially into glucose-1-phosphate and then into glucose-6-phosphate. Thus the product of the first enzymatic reaction became the substrate of the second. Pittman and coworkers attempted to apply this concept to "heterogenised" TMC. In order to elucidate the nature of the influence of different "heterogenised" TMC on one another, catalysts were prepared[102] by the joint coordination of different metal complexes on a polystyrene–divinylbenzene copolymer containing phosphino-groups and by mixing catalysts prepared beforehand; the hybrid catalysts investigated are listed below.

The oligomerisation of buta-1,3-diene was the model reaction in the studies of Pittman and coworkers. The data obtained for the activity of catalyst (IV) and the proportions of the reaction products were satisfactorily reconciled with those obtained earlier[107,108] for the activity of the homogeneous $(PPh_3)_2Ni(CO)_2$ catalyst. The complete correspondence of the homogeneous-catalytic reaction to the heterogeneous-catalytic process was explained[102–105] by the absence of steric hindrance for the small molecule of the diene hydrocarbon.

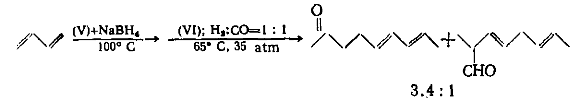
Catalyst (V), reduced by two equivalents of $NaBH_4$ to give polymer-bound zero-valent nickel, retained 90% of its activity and proved to be highly selective (98%) in the linear dimerisation of buta-1,3-diene[109]:





This result is inconsistent with data obtained in a study of the activity of the homogeneous $(PPh_3)_2NiBr_2$ catalyst[110], in the presence of which a whole series of products are obtained.

When catalyst (V) modified by sodium tetrahydroborate is mixed with catalyst (VI), an active catalyst, which selectively oligomerises and hydroformylates buta-1,3-diene, is obtained:



The combination of the oligomerising catalyst (IV) with the hydrogenating catalyst (VI), which has been suggested as catalyst (VII) on a common matrix, proved to be successful:

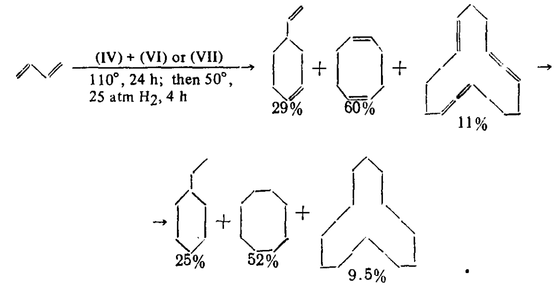


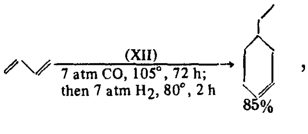
Table 2. Comparison of the rates of hydrogenation of 1,5-COD in the presence of the hybrid and homogeneous $Ir(CO)Cl(PPh_3)_2$ catalysts in benzene (170°C; 10 atm).

Catalyst	P:Ir	Total *P* content on polymer, wt.%	Time, h	Conversion	
				cyclooctene, %	cyclooctane, %
Homogeneous	3	—	33	37	3
Hybrid	3	4.02	0.25	57	4
Homogeneous	4	—	48	44	3
Hybrid	4	10.28	0.25	69	5
Homogeneous	6	—	72	68	11
Hybrid	7	4.02	93	5	0
Hybrid	7	1.25	0.20	68	6
Homogeneous	14	—	72	50	1
Hybrid	12	2.53	94	19	2
Hybrid	12	4.02	96	6	0
Homogeneous	22	—	72	15	0
Hybrid	22	4.02	93	18	2

By employing different version of hybrid catalysts based on $(PPh_3)_2Ni(CO_2)_2$ and $(PPh_3)_2RuCl_2(CO)_2$ [(IV) + (X)], it proved possible to obtain mono-olefins with a high degree of selectivity via the oligomerisation stage. It is noteworthy that homogeneous catalysts propagate the process analogously under the same conditions.

By varying different catalysts, Pittman and coworkers[102] obtained complete and partial hydrogenation, oligomerisation, and hydroformylation products from buta-1,3-diene, and the hybrid catalyst, obtained on a common matrix and carrying two different catalytically active groups, propagated the process in the same way as the catalyst obtained by mixing two complexes made heterogeneous separately.

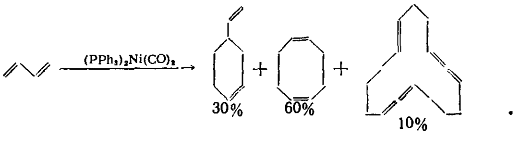
The observation of the process



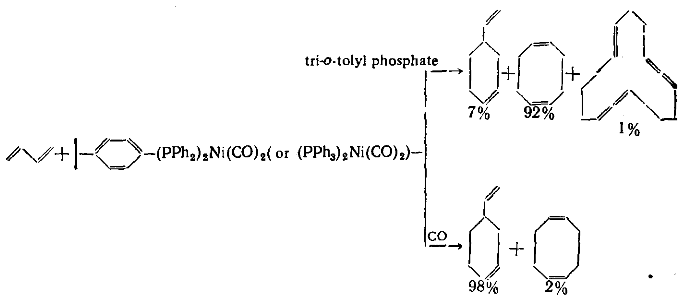
which occurs on catalyst (XII) with high yields, must be recognised as one of the most important results obtained[102].

The attainment of a high selectivity of the hybrid catalysts which propagate a consecutive multistage catalytic process increases significantly the effectiveness of such systems; this explains the attention which Pittman and coworkers[109,111,112] devoted to the preparation of selective oligomerisation and hydrogenation catalysts.

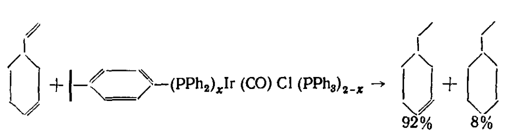
Conditions under which butadiene selectively dimerises either to 4-vinylcyclohexene (4-VCH) or to cyclo-octa-1,5-diene have been described[111]. The proportions of the butadiene oligomerisation products in the presence of the $(PPh_3)_2Ni(CO)_2$ homogeneous catalyst may be represented as follows[107,108]:



The promotion of this homogeneous catalyst or its "heterogenised" analogue by carbon monoxide or phosphite may alter significantly the selectivity of the catalytic system:

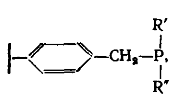


A catalyst capable of the selective propagation of the hydrogenation stage—the Vasko's complex "heterogenised" on a phosphinated styrene–divinylbenzene copolymer, i.e.



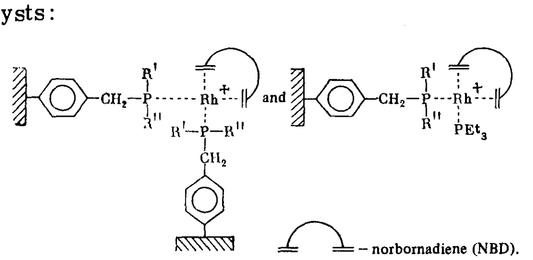
has been proposed[111] and the possibilities of this selective hydrogenation catalyst have been studied in detail[111,112].

By varying the substituents at the phosphorus atom of the polymer matrix, Graziani and coworkers[113,114] attempted to obtain a high selectivity of a hybrid phosphino-polymer catalyst, on which a transition metal complex had been deposited, in the hydrogenation of the double bond and the carbonyl group:



$$\text{—}C_6H_4\text{—}CH_2\text{—}P(R')(R'')$$

where R′ = R″ = Ph, or R′ = Me and R″ = Ph, or R′ = menthyl and R″ = Ph. The rhodium complexes [Rh(NBD).(acac)] and $[Rh(NBD)(PEt_3)_2]^+$ were fixed on the surface of the matrix, which resulted in the formation of the following catalysts:

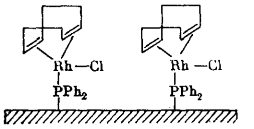


These deposited catalysts proved to be selective in the hydrogenation of the carbonyl group and the double bond of the olefin. It was noted[113,114] that the increase of the basicity of the phosphine coordinated to the rhodium atom increases the activity of the catalyst in the reduction of the carbonyl group, diminishing at the same time its activity in the hydrogenation of the olefin. It is noteworthy that in the study of the reduction reaction certain results may be partly distorted owing to the presence of the liberated metal.

Dumont et al.[115] investigated yet another ketone conversion reaction—catalytic hydroxylation. The hybrid catalyst consisted of a rhodium(I) complex "heterogenised" on a complex polymer matrix. The effectiveness of this catalytic system proved to be very similar to that of the corresponding homogeneous system. The possibility of repeated utilisation of the heterogeneous catalyst was noted as its main advantage.

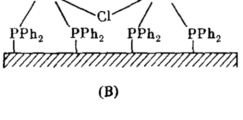
In conclusion we shall examine the structure of the active centres in the hybrid catalysts obtained. When complexes are "heterogenised" there is a possibility of two types of binding, in the first of which the phosphinated polymer plays the role of a monodentate macroligand, and in the second it chelates the TMC. It is noteworthy that this question is not as yet entirely clear.

Thus, on "heterogenising" the same complex $[RhCl(COD)]_2$ on phosphinated polystyrene, Collman et al.[89] and Grubbs et al.[116] reached different conclusions concerning the nature of the binding of the transition metal to the polymeric macroligand. According to Collman et al.,[89] when this complex is "heterogenised" on cross-linked (to the extent of 2%) polystyrene, the process reduces to the rupture of a Cl bridge, and the formation of the adduct

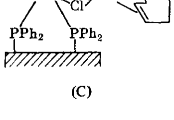


(A)

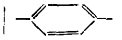
Grubbs et al.[116] established that, when the complex is "heterogenised" on a polymer with the same degree of cross-linking, two moles of COD are liberated per mole of the TMC, which may be represented by the surface structure B. For higher degrees of cross-linking of the polymer (20%), the way in which the rhodium complex is rendered heterogeneous alters, since 1.4 moles of cyclo-octadiene are evolved per mole of the adsorbed compound, which can be accounted for by the formation of the set of surface structures B and C:

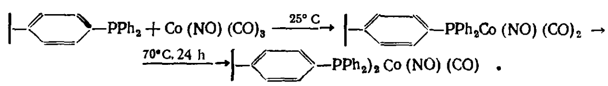


(B)



(C)

A study of the coordination of carbonyl TMC on phosphinated polystyrene matrices established[89,93] that, although in the majority of cases chelation by the carrier takes place, in certain cases a mixed type of coordination occurs [for example, when the complex $Rh_4(CO)_{12}$, to the active centres of which the structure  $(PPh_2)_{1.5}.$ $.Rh_4(CO)_{10.5}$ has been attributed, is made heterogeneous[80]] as well as monodentate binding, which may be transformed into chelate binding under more severe conditions[89]:



Collman et al.[89] also described the possibility of tridentate binding of the complex $RhCl(PPh_3)_2(CH_2 = CH_2)$ by the polymeric macroligand, which leads to the formation of a complete polymeric analogue of Wilkinson's complex.

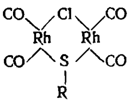
Thus one may conclude that the structure of the surface centres in the "heterogenised" complexes may depend on (1) the nature of the polymer, the structure of its surface group, and the degree of cross-linking, (2) on the composition and structure of the "heterogenised" transition metal complex, and (3) on the conditions under which the complex is "heterogenised".

V. THE BINDING OF TRANSITION METAL COMPLEXES TO OTHER POLYMERIC MACROLIGANDS

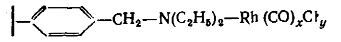
The preparation of hybrid catalysts based on polymers with phosphino-groups was examined above. Attempts have been made to achieve the coordination of the complex also to other groups.

The conversion of olefins into aldehydes and alcohols in the presence of rhodium-containing complexes on *p*-substituted polystyrenes, where the substituents were $-N(CH_3)_2$, $-CH_2N(CH_3)_2$, $-P(C_4H_9)_2$, $-CH_2PPh_2$, or -SH, has been studied[117] and it has been found that the hybrid catalysts and their homogeneous analogues have approximately the same selectivities in the formation of aldehydes. The phosphinerhodium complexes exhibited a very high selectivity in the formation of an aldehyde, while the aminerhodium complexes showed a high selectivity in the formation of an alcohol. On the other hand, the activity of the hybrid amino-catalyst in the above reaction proved to be much higher than that of its homogeneous analogue.

The cleavage of the dimeric rhodium complex $[Rh(CO_2)Cl]^2$ by monomeric amines and phosphines has been investigated[118]. When the complex was rendered "heterogenised" on a polymer, a hybrid catalyst propagating the hydrogenation and hydroformylation reactions was formed. The study of the influence of monomeric and polymeric thiols on the cleavage of the heterogeneous complex showed that monomeric thiols do not cleave the complex molecule, giving rise to $[Rh(CO)_2RS]_2$, while polymeric thiols yield a product having the following structure:



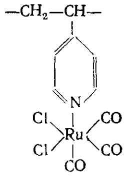
Mitchell and Whitehurst[92] rendered a rhodium carbonyl complex heterogeneous on a polystyrene polymer containing ethylamino-groups:



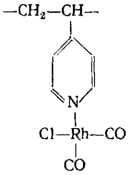
The catalyst thus obtained showed a very low activity in the hydrogenation of methyl linoleate, but exhibited an exceptionally high selectivity in the selective hydrogenation of a single double bond: it propagates the hydrogenation of terminal double bonds significantly faster than that of inner double bonds.

Moffat's studies[119,120] led to new possibilities in the employment of finished polymers as matrices for the fixation of transition metal complexes in order to obtain hybrid catalysts. When cobalt carbonyls were made heterogeneous on poly-2-vinylpyridine, it proved possible to obtain an active hydroformylating system and it was established that only approximately 40% of the nitrogen atoms of the polymeric carrier are capable of participating in complex formation with cobalt carbonyl. The hydroformylation of hex-2-ene in the presence of such a system at 165–170°C takes place to the extent of 50% (p = 124 atm, $H_2 : CO = 1:1$).

Braca et al.[121] prepared a hybrid catalyst by attaching the complexes $[RuCl_2(CO)_3]_2$ and $[RhCl(CO)_2]_2$ to linear poly-4-vinylpyridine (P4VP):

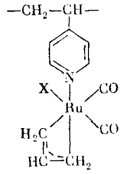


(XIII)



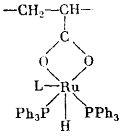
(XIV)

However, the metal-polymer complex catalysts obtained proved to be relatively inactive and operated only under very severe conditions. Thus the first of two catalysts (XIII), used in the synthesis of ethers from propene, CO, and methanol, propagated the process at 30 atm and 190°C. Under these conditions, the complex was rapidly split off from the polymeric matrix and the polynuclear complex $Ru_3(CO)_{12}$ was formed[122]. In an attempt to obtain a higher activity of a hybrid ruthenium complex catalyst, the authors[123,124] fixed the $RuCl(\pi-C_3H_5)(CO)_3$ and $RuBr(\pi-C_3H_5)(CO)_3$ complexes[123,124] to P4VP and the complex $RuH_9(PPh_3)_3L$ (where L = PPh_3 or CO) to polyacrylic acid:



(X = Cl, or Br)

(XV)



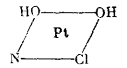
(XVI)

(L = PPh_3, or CO).

The hybrid catalyst (XV) proved to be active under relatively mild conditions (100°C) in many reactions employing unsaturated hydrocarbons as substrates (for example, in the isomerisation of but-1-ene), the complex remaining attached to the polymer under the reaction conditions. By comparing the activities of hybrid complexes (XV) with their homogeneous analogues in the isomerisation of but-1-ene, Braca et al.[121] established that, while their selectivity remains the same, the activity of the catalysts deposited on the polymer is in many cases higher than that of the homogeneous TMC. In the isomerisation and hydrogenation of pent-1-ene in the presence of complex (XVI) the hybrid catalyst is significantly less active than its homogeneous analogue, which the authors attributed to the steric hindrance to the reaction arising in the presence of the polymeric catalyst.

A whole series of catalysts for the hydrosilylation of alkenes, alkynes, and alkadienes, active in liquid and gaseous phases, have been prepared[84,125-129] by "heterogenising" certain TMC (for example chloroplatinic acid and tetracarbonylrhodium dichloride) on styrene–divinylbenzene copolymers with surface dimethylamino- and cyano-groups.

Studies of the catalytic properties of platinum, iridium, rhodium, and palladium chloride complexes deposited on nylon (where the transition metal atom is coordinated to the nitrogen atom of the peptide group in nylon) in the hydrogenation of benzene established[130-132] that, in order to obtain an active catalyst, the presence of a hydroxy-group in the coordination sphere of the complex is necessary. The structure of the catalytically active platinum complex obtained by depositing H_2PtCl_6 on nylon is[130]



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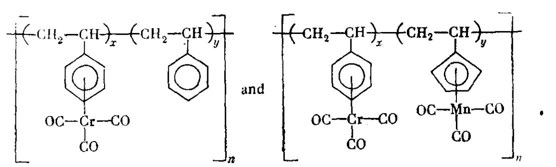
When the catalytic activities of metal–nylon complexes with respect to benzene hydrogenation products, referred to 1 gram-atom of the metal, are compared, the metals can be arranged in the following sequence: Ir > Pt > Rh > Pd.[132]

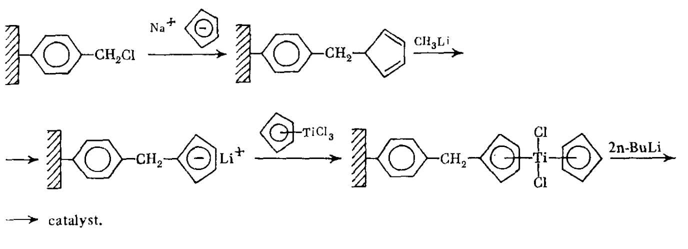
One must note that the hydrogenation of metal-complexes on a polymeric support does not always lead to the formation of a hybrid catalyst. Thus Kraus and Tomanova[133], who attached $PdCl_2$ to a styrene–divinylbenzene copolymer containing $-CH_2-CN$ surface groups, did not obtain a catalyst active in relation to olefins.

Transition metal complexes can be bound to a polymeric matrix by a procedure other than via heteroatomic groups specially introduced into the polymer and coordinating the transition metal. For example, by employing the benzene rings of polystyrene as a π-coordinating agent and synthesising polymers with a specified structure, Pittman and coworkers[124,125] obtained complexes having the following composition:

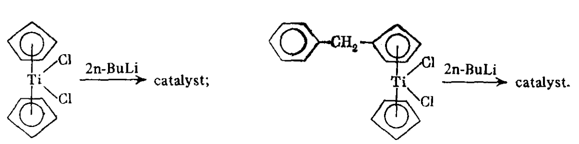


The first catalytic system proved to be active in the selective hydrogenation of methyl sorbate to methyl-3-hexenoate in cyclohexane at 160°C and 35 atm.[134]

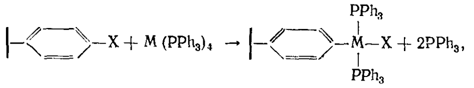
Grubbs et al.[116] synthesised a styrene–divinylbenzene copolymer with attached titanocene, which was thus made heterogeneous:



This system proved to be six times more active in the hydrogenation of cyclohexene than the corresponding homogeneous catalytic systems:



Mizoroki et al.[136] proposed a new method for converting transition metal complexes into heterogeneous systems on a polymer by the formation of a σ-bond between the transition metal atom and a carbon atom in the polymeric matrix. This approach is based on studies[137-139] in which σ-aryl complexes of nickel, palladium, and platinum were obtained by the oxidative addition of an aryl halide to the corresponding tetrakis(triphenylphosphine) complexes of transition metals. The reaction with halogenated polystyrene was carried out as follows[140]:



where M = Ni, Pd, or Pt and X = Br or I.

The complexes prepared in this way were treated with boron trifluoride etherate in the presence of small amounts of water and were investigated as catalysts of the dimerisation of ethylene and propene[136,141]. The former reaction was studied using the catalyst in the liquid phase and the latter was studied in the vapour phase in the presence of a hybrid catalyst—activated by BF_3OEt_2/H_2O (in proportions of 10 : 1). As regards the nature of the catalytic activity, these systems are identical with their low-molecular-weight analogues, although their activities are somewhat lower.

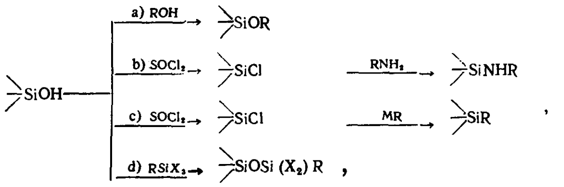
VI. CONVERSION OF TRANSITION METAL COMPLEXES INTO HETEROGENEOUS SYSTEMS ON MINERAL CARRIERS

The employment of polymeric carriers in order to convert TMC into heterogeneous systems makes it possible to apply a wide variety of synthetic methods. However, all the above catalysts suffer from one common disadvantage: the polymeric base of the systems is responsible for their low thermal stability and low resistance to the action of oxidants. Mineral carriers are free from this disadvantage. Studies dealing with the deposition of TMC on mineral carriers can be divided into two groups: (1) conversion into a heterogeneous system via a coordination reaction using organosilicon compounds as agents fixing the TMC to the surface; (2) conversion of TMC into heterogeneous systems directly on the mineral carrier via the functional groups of the latter.

The most widely used mineral carrier is coarsely porous silica gel subjected to preliminary hydroxylation, although it has been stated[142-144] that alumina gel and crystalline and amorphous aluminosilicates have been used to "heterogenise" TMC.

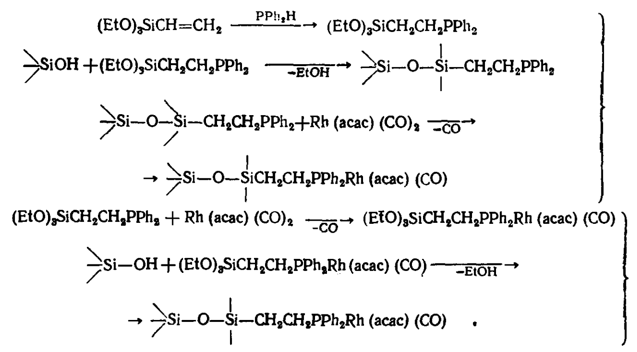
1. Conversion into Heterogeneous Systems Using Organosilic Compounds

Functional groups can be grafted to silica gel in several ways:



where R is an organic hydrocarbon group, X a readily hydrolysable group such as Cl, OR, or OCOR, and MR an organometallic compound such as LiR or XMgR. The synthesis of macroligands for hybrid catalysts by methods (a)–(c) has not been described in the literature, but there are data concerning the preparation of a carrier for TMC by method (d), which is probably due to the greater thermal stability and greater resistance to hydrolysis of the Si–C bond compared with those of the Si–O–C and Si–N–C linkages. Furthermore, the attachment of the functional group by method (d) can be readily achieved in a single stage under mild conditions and makes it possible to employ a large set of modifying agents.

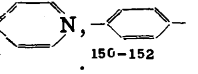
The investigations of Allum and coworkers[145–153] of the preparation of hybrid catalysts based on silanised silica gel must be regarded as the first studies of this kind. Such catalysts are synthesised in accordance with the following schemes[145,149]:



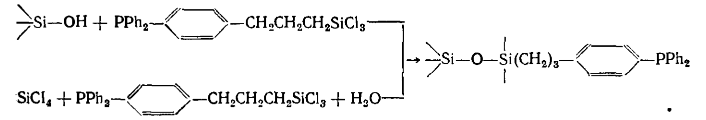
(4)

(5)

It is noteworthy that not only the rhodium acetylacetonate complex but also other rhodium, palladium, and platinum complexes may be converted into heterogeneous systems[152].

The catalysts prepared in this way were used in hydrogenation and hydroformylation processes[145,150], but their activity was somewhat lower than that of the corresponding low-molecular-weight analogues. By "heterogenising" other transition metal complexes, the limits of the applicability of such heterogeneous catalysts are expanded and they can be used for the isomerisation and acetoxylation of olefins, for the oligomerisation of dienes, for the polymerisation and cyclo-oligomerisation of acetylenes[149], and for the hydrosilylation of olefins[151–153]. Apart from the phosphino-group, the following "anchor" groups have been used: $-CH_2CH_2CN$, $-CH_2CH_2CH_2NH_2$, $-CH_2CH_2CH_2NEt_2$, $-CH_2CH_2CH_2SH$, $-CH_2CH_2CH_2CH_2-$  $CH_2N(CH_2PPh_2)_2$, and $-CH_2CH_2CH_2N$.[150–152]

Moreto et al.[90] prepared a phosphine-containing silica gel matrix to which they subsequently coordinated $RhCl(PPh_3)_3$ and $[RhCl(C_2H_4)_2]_2$:



The study of the catalytic activity of rhodium complexes fixed on a phosphinated silica gel support in the hydrogenation of *p*-menth-1(7)-ene showed that the ratio of the *cis*- and *trans-p*-menthanes obtained in the reaction is 9.2 : 1, which indicates a higher selectivity of the catalyst compared with homogeneous Wilkinson's catalyst and the rhodium complex "heterogenised" on polystyrene (see Section IV)[90].

Thus one may claim that in many instances a fairly high process selectivity may be achieved on synthesising hybrid catalysts by coordinating TMC to a phosphinated silica gel.

Comparison of the catalytic activities of complexes "heterogenised" on a phosphinated polymer and on a mineral carrier, which makes it possible to estimate the influence of the support on the catalytic properties of the systems, is of great interest. The data of Michalska and Webster[154], who established that the rate of hydrogenation of pent-1-ene in the presence of $RhH(CO)(PPh_3)_3$ attached to a phosphinated silica gel is six times higher than in the presence of a complex bound to a polystyrene matrix, provides one of the few examples of such a comparison. The authors[154] explained this effect, which has been observed also by other investigators[80,103], by the hindered diffusion of the substrate molecules to the active centres within the polymer pores. Furthermore, they established[154] that the activities of the complex $RhH(CO)(PPh_3)_3$ "heterogenised" on silica gel and its homogeneous analogue are virtually indistinguishable. The rates of hydrogenation of pent-1-ene are in proportions of 1.3 : 1.4. Similar results were also obtained in another investigation[80].

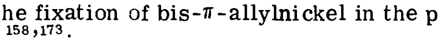
We believe that the similarity in the behaviour of catalysts "heterogenised" on silica gel and the homogeneous catalysts can be explained by the fact that the silicon–hydrocarbon support to which the complex is attached creates conditions for the additional mobility of the active centre, as a result of which the properties of the "heterogenised" complex on a mineral support approach those of the homogeneous complex and differ from the complex bound to a polymer.

2. Conversion into a Heterogeneous System with Formation of a σ-Bond between the Transition Metal and the Carrier

The disadvantages of the preparation of hybrid catalysts by the method described above include the large number of stages in the synthesis and its long duration as well as insufficient stability of the bond between the TMC and the matrix. These disadvantages may be eliminated by the direct interaction of TMC with the mineral carrier, which results in the formation of stable σ-bonds between the central metal atom and the carrier.

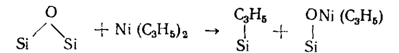
The first studies in this field include those described in Refs.155–158. Here we shall only mention that, by modifying the surface of aluminosilicate with tris-π-allylchromium, Shmonina and Stefanovskaya prepared a catalyst which proved to be active in the *trans*-1,4-polymerisation of butadiene and isoprene. Subsequently the copolymerisation of butadiene and isoprene was achieved in the presence of the same catalytic system[159,160].

Detailed systematic studies have been made on the structures and catalytic activities of catalysts obtained by modifying mineral carriers with π-allyl complexes of transition metals[158,161-170,172-187]. A general method for the preparation of such catalysts has been examined in relation to the fixation of bis-π-allylnickel in the presence of silica gel[158,173]:

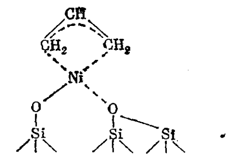


$$\geqslant Si-OH + Ni(C_3H_5)_2 \rightarrow \geqslant Si-O-Ni(C_3H_5) + C_3H_6 \ .$$

It was shown that this is the main type of binding, involving the elimination of one propene molecule, although at a higher concentration of the organometallic compound or in the presence of silica gel heated at a higher temperature, binding to the oxygen groups of the carrier is possible (see also Skupinsky and Malinovski[188]):



Square coordination obtains in a surface organonickel complex:



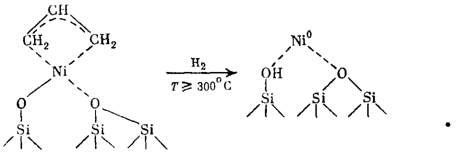
Ermakov et al.[161] established an interesting feature of the π-allyl linkage in the surface complex. They found that, in terms of a number of properties, it differs significantly from the linkage in bis-π-allylnickel, being thermally more stable, but at the same time showing a greater tendency towards hydrolysis. Thus the heterogeneous complex reacts with water at 20°C to give propene.

It has been shown[158] that surface compounds may be used as catalysts of different processes in three states.

1. In the initial state, i.e. directly after treating the carrier with the π-allyl complex. Such surface coordination compounds can serve as active centres in the polymerisation of olefins and dienes[162-164,166,167] and the disproportionation of olefins (propene)[168,169,184]. Comparison of the catalytic activities of hybrid catalysts with those of their homogeneous analogues showed that, whereas bis-π-allylnickel[170] and tetrakis-π-allylmolybdenum[171] do not induce the polymerisation of butadiene, the allyl complex of nickel deposited on silica gel gives rise selectively to the *cis*-1,4-polymer, $Ni(C_3H_5)_2/Al_2O_3$ produces the *trans*-1,4-polymer, while $Mo(C_3H_5)_4$ deposited on carriers gives rise to a polymer having a mixed structure. Furthermore, butadiene is known to polymerise in the presence of π-allylnickel halides with the preferential formation of the *trans*-1,4-polymer[172], while the π-allylnickel halide system on silica gel induces *cis*-1,4-polymerisation[162].

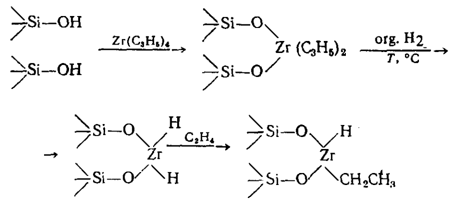
Thus one may claim that hybrid catalysts are more capable of increasing significantly the activity and of altering the selectivity, compared with their homogeneous analogues.

2. In the reduced state, where the low-valence state of the transition metal atom is stabilised by the surface groups of the carrier. The reduction of the surface allyl complex of nickel is described by the scheme

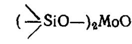


It is of interest that the stabilisation of nickel atoms by the oxygen atoms of the silica gel matrix is so pronounced that it protects them from further agglomeration to large crystals. This follows from data obtained in a study of the magnetic susceptibilities of specimens of nickel catalysts[158]. The catalysts obtained in the reduced state proved to be active in hydrogenation reactions[158,173], while a deposited and reduced molybdenum complex was active in ammonia synthesis[174].

An interesting study has been made on the stabilisation of highly dispersed platinum on silica gel (obtained after the deposition and reduction of π-allyl complexes) by molybdenum prepared similarly. The formation of Pt-Mo clusters has been suggested and then proved by X-ray photoelectron spectroscopy; such clusters protects the platinum atoms from further migration and agglomeration to form crystals[180,183]. A catalyst of the polymerisation of ethylene, whose structure and the mechanism of its action have been determined mass-spectrometrically, has been prepared in the reduced state by depositing tetrakis-π-allylzirconium on silica gel[175,176]:



3. A hydrogen oxidation catalyst has been prepared in the oxidised state[165]:



$$(\geqslant SiO-)_2MoO_2 \ .$$

Not only allyl complexes of transition metals but also their chloride complexes have been "heterogenised"[166]; the $TiCl_3/SiO_2$ catalyst proved to be active in the polymerisation of ethylene. Studies[189,190] on the polymerisation of ethylene on "heterogenised" cyclopentadienyl, arene, and allyl complexes of chromium are closely related to those of Ermakov and coworkers[165,166]. Zhorov and coworkers[191,192] employed the same approach as Ermakov and coworkers[165,166] and deposited benzonitrilepalladium complexes on silica gel. In their earlier study of the activity of these compounds in homogeneous systems[193,194] they had established that the complex $(PhCN)_2PdCl_2$ is exceptionally active in the migration of the double bond and that the addition of methanol appreciably accelerates this reaction. A significant disadvantage of the introduction of methanol into the system is rapid decomposition of the complex with liberation of metallic palladium.

Zhorov et al.[191] established that the complex attached to silica gel is 100 times more active in the isomerisation of pent-1-ene than its homogeneous analogue and that the introduction of methanol into the heterogeneous system does not affect its activity. The results led to the hypothesis that the deposition results in the formation of the stable complex $>$Si-O-PdClLL′ or $>$Si-O-PdClL$_2$ (where L′ = benzonitrile and L = labile olefin ligand), while in the presence of methanol added to the homogeneous system, unstable compounds having the composition CH$_3$O-PdClL$_2$ are formed.

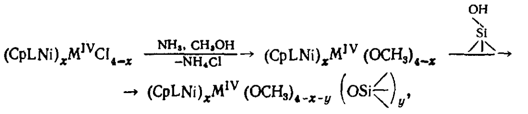
The study of the activities of hybrid catalysts demonstrated a distinct maximum at a specific metal complex concentration, which was explained by an optimum amount of (PhCN)$_2$PdCl$_2$ for hydrogenation, above which the reaction

$$2L'_2PdCl_2 + 2L \rightarrow (LPdCl_2)_2 + 4L',$$

takes place, and the benzonitrile liberated as a result competes in coordination, lowering the overall activity of the catalyst.

It is noteworthy that the results of Zhorov et al.[191] require further confirmation, since only exact data on the structure of the surface groups make it possible to demonstrate unambiguously the structure of the catalyst.

Another approach was used by Lisichkin and coworkers[195-198] in the preparation of hybrid catalytic systems, the essential feature of which is that complexes of nickel bound to a Group IVA element are used as the organometallic compounds:



$$(CpLNi)_xM^{IV}Cl_{4-x} \xrightarrow[-NH_4Cl]{NH_3,\ CH_3OH} (CpLNi)_xM^{IV}(OCH_3)_{4-x} \xrightarrow{\text{HO-Si}} \rightarrow (CpLNi)_xM^{IV}(OCH_3)_{4-x-y}\left(OSi\lessdot\right)_y,$$

where L = PPh$_3$, PBu$_3$, or CO, M^{IV} = Si, Ge, or Sn, x = 1 or 2, and y = 1, 2, or 3. The strength of the Ni-M^{IV} and M^{IV}-O bonds is responsible for the absence of the aggregation of nickel atoms on the silica gel surface up to 250°C. Treatment of the fixed complexes with hydrogen at an elevated temperature leads to partial elimination of the ligands and to the appearance of catalytic activity.

Since tin and germanium can combine not only with one but also with two nickel atoms, Lisichkin et al.[198] were able to compare the activities of mono- and di-atomic nickel centres in the hydrogenation of olefins. It was found that catalysts with diatomic centres are not only more active but also more stable.

By varying the nature of the ligands at the nickel atom, it was possible to alter specifically the selectivity of the catalysts. Thus it was shown[197] that the usual impregnated nickel catalyst, modified with triphenylphosphine, exhibits the same selectivity as the triphenylphosphine-nickel complex fixed on silica gel.

VII. INCORPORATION OF METAL COMPLEXES IN POLYMER GELS

In 1971, Kabanov[199] suggested that the catalytic systems consisting of grains of polymer gels in the bulk phase of which the corresponding active centres are immobilised be used as catalytic systems. A characteristic feature of such catalysts is the possibility of the occurrence of reactions not only on the surface of the grain, but also throughout the bulk of the swollen polymer particle. In such systems the effectiveness of the utilisation of the active centres should be just as high as in heterogeneous catalysts. At the same time the reaction products should be readily removable from the catalytic gel.

Subsequently Kabanov and coworkers[200] undertook a series of studies devoted to the formation of metal complex gel-like polymerisation catalysts. They showed that catalysts of this type exhibit a high stability, polymerising, for example, ethylene at elevated temperatures up to 200°C, i.e. under conditions where the usual catalysts of the Ziegler-Natta type are deactivated very rapidly. After the catalyst had been used for 2000 h, virtually no decrease of activity was observed. The yield of the polymer after this period may reach up to 500 kg per gram of the transition metal. It is extremely significant that the polyethylene obtained in the presence of gel-like catalysts contains virtually no transition metal compounds, i.e. does not require washing. Each catalyst grain consists in essence of a tiny reactor from which the polymer formed diffuses to the surrounding solution, while the metal compounds forming part of the composition of the active centre remain firmly bound inside.

The use of catalytic systems of this kind requires, however, particular attention to processes involving the diffusion of the reaction product from the gel-like particle. Clearly, in the synthesis of polymer molecules with a high molecular weight the reaction rate begins to be limited by the rate of diffusion.

The literature data presented in this review show that the "heterogenised" TMC are likely to be very useful in catalysis. Despite the fact that there is still a long way to go before a detailed understanding of the action of deposited metal catalysts is achieved, certain important conclusions may already be made.

Fixation of TMC on mineral and polymeric carriers to form heterogeneous systems makes it possible to retain to a large extent the activity and selectivity of the corresponding homogeneous catalysts.

In many instances conversion into heterogeneous systems, makes it possible to increase significantly the activity of the homogeneous catalyst owing to the greater stability of the coordination-unsaturated state of the transition metal atom on the surface and the absence of agglomeration of the active particles.

Conversion of TMC into a heterogeneous form gives rise to great possibilities for the development of catalysts with the structure of active centres specified beforehand by varying the nature of the metal, the mode of binding to the carrier, the nature of the ligand, etc.

The improvement of methods for the conversion of TMC into heterogeneous systems will apparently make it possible to synthesise heterogeneous catalysts with complex but entirely identical active centres, i.e. to solve the problem of the formation of catalysts the selectivity of the action of which is similar to that of enzymes.

During the period when the manuscript was with the editors, numerous new studies devoted to "heterogenising" TMC on both organic and mineral carriers were published. A fairly complete list of publications on the "heterogenisation" of TMC up to the middle of 1977 is given in the bibliographic guide published by the Institute of Catalysis of the Siberian Division of the USSR Academy of Sciences[201]. The great interest of investigators in the problem of the synthesis and study of hybrid catalysts is indicated by the proceedings of the conferences held in Novosibirsk (June, 1977)[202] and Lyons (November, 1977)[203]. One can apparently conclude that heterogeneous metal complex catalysis is one of the principal fields in which modern catalytic chemistry will develop.

Analysis of studies published recently shows that the following main trends have arisen: (1) the synthesis of hybrid catalysts without homogeneous analogues; (2) the development of methods of synthesis of bi- and polyfunctional catalysts; (3) the use of organometallic compounds for the synthesis of highly dispersed deposited metallic catalysts; (4) the conversion of metal complex cluster compounds into a heterogeneous form.

One should bear in mind that the possibilities of catalysis by transition metal complexes fixed on a surface have been by no means fully utilised. The use of hybrid catalysis containing a fixed chiral centre has given rise to considerable possibilities for asymmetric catalytic synthesis.

There have been virtually no studies concerning the application of metal complex catalysis to processes which can be achieved only at elevated temperatures. The use of stable "heterogenised" complexes on mineral carriers will make it possible to solve this problem.

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Advances in the Chemistry of Verdazyl Radicals

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Data relevant to the methods of synthesis of various verdazyl mono-, bi-, tri-, and poly-radicals as well as their analogues (tetra-azapentenyl, tetrazolinyl, and phototetrazolinyl radicals) are discussed, and the reactions of verdazyls not involving the free valence are considered; data are presented on the structures, spectra, and physical and chemical properties of verdazyls. Attention has been concentrated on problems of the kinetics and mechanisms of chemical reactions involving verdazyls. Problems of the practical applications of verdazyls in chemical, physical, and biological research (inhibition of free-radical reactions, stabilisation of polymeric materials, spin labels, redox indicators, galvanic cells, etc.) as well as the prospects for the development of this new class of stable radicals are discussed.

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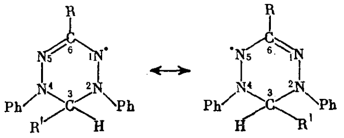
I. INTRODUCTION

Verdazyls (tetrahydrotetrazinyls) occupy a special place amonst stable radicals. The striking stability of verdazyls, the ease with which their reactions may be studied by spectroscopic methods, and their ready solubility make them suitable objects for the solution of many chemical and physicochemical problems. Since the discovery of verdazyls by Kuhn and Trischmann[1-3] (1963), more than 150 papers have been published on the synthesis, structures, and physicochemical properties of verdazyls. Certain aspects of the chemistry and physicochemical properties of verdazyls are dealt with in a number of publications[4-6].

In the present review attention has been concentrated on the structures, methods of synthesis, reactivities, and practical applications of verdazyls; other problems (EPR, NMR, and quantum-chemical calculations) are dealt with in less detail.

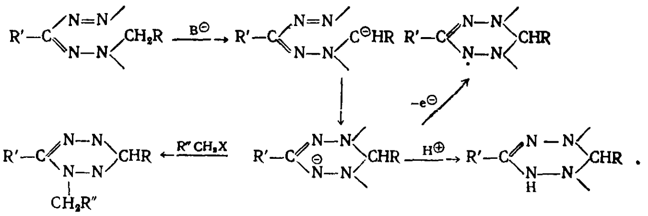
II. METHODS OF SYNTHESIS OF VERDAZYLS

Verdazyls were discovered in studies on the alkylation of formazans[7,8]. A characteristic feature of verdazyls is the obligatory presence in the 2- and 4-positions of aromatic substituents (the substituents at the carbon atoms in the 3- and 6-positions may be varied[9,10]):

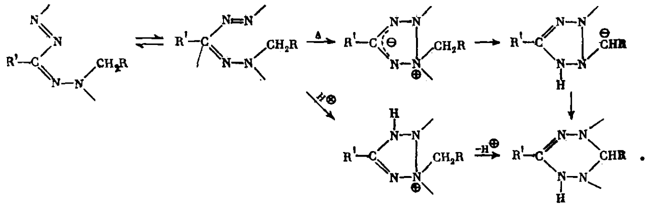


(I) $R' = H, R = Ph$;
(II) $R' = H, R = p\text{-}X\text{-}C_6H_4$;
(III) $R' = CH_3, R = Ph$;
(IV) $R' = H, R = (CH_3)_3$.

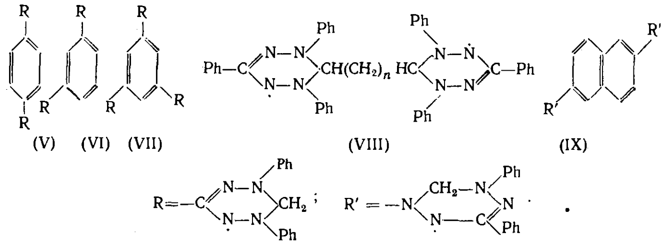
The alkylation reaction is the main method for synthesising verdazyls. The cyclisation of *N*-alkylformazans with the formation of tetrahydro-*syn*-tetrazines (leucoverdazyls), which constitutes formally the addition of the alkyl group to the –N=N– bond, has been studied in detail[11]. The capacity of *N*-alkylformazans for cyclisation depends greatly on the size of the substituents at the central carbon atom, which influences the *trans*-(*anti*-*syn*) isomerisation of formazans[12,13]. Bulky substituents (phenyl, t-butyl) tend to fix the chelate form with a strong intramolecular hydrogen bond, while alkyl substituents weaken the hydrogen bond and lead to the opening of the chelate ring (*trans*-*anti*-form). Thus the energy of the intramolecular hydrogen bond is approximately 7 kcal mole^{-1} in triphenylformazan and approximately 2 kcal mole^{-1} in diphenylformazan[14]. The cyclisation of *N*-alkylformazans can proceed under the influence of strong bases (NaOH, t-BuK, $NaOC_2H_5$), acids, or thermally. The *N*-alkylformazan anion formed under the influences of bases cyclises to the leucoverdazyl anion, which undergoes further transformations:



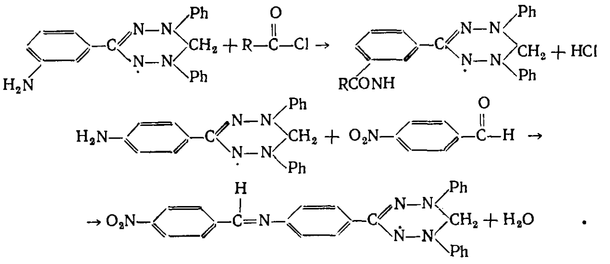
The rate of thermal cyclisation of *N*-alkylformazans follows first-order kinetics and increases rapidly with temperature ($\Delta H = 25$ kcal mole^{-1}). It is suggested[11] that the rate-limiting stage in such cyclisations is the formation of a delocalised zwitter-ion, which is converted into the isomeric ylid and then into the leucoverdazyl via the Stevens rearrangement. The ease of cyclisation of *N*-alkylformazans under the influence of acids is associated with the formation of a protonated form of the delocalised zwitter-ion:



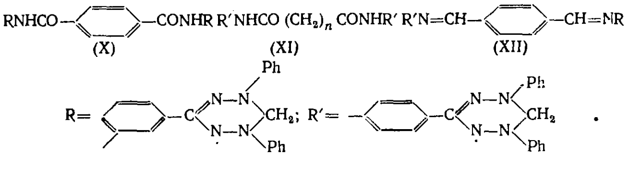
Under the influence of oxidants [$FeCl_3$, $K_3Fe(CN)_6$, PbO_2], leucoverdazyls are dehydrogenated to verdazyls. In many cases *N*-alkylformazans are stable[15-17] and cyclise only at high temperatures. Under the influence of alkalis, verdazyl salts may recyclise[9,18,19]. Compound (I) is also obtained by the reduction of tetrazolium salts with diazomethane[9]. Verdazyls can give rise to bi- and tri-radicals by being joined together in the 3-, 6- and 4-positions:


(V) (VI) (VII) (VIII) (IX)

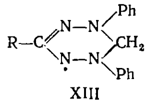
Many mono-, bi-, and tri-verdazyls have now been synthesised from the corresponding formazans[20-23]. Aminoalkylation of formazans yields verdazyls with amino-groups in the 3-position[9]. It has been found recently[24] that 6-aminoverdazyls may be acylated by acyl chlorides or may be converted into imines by reaction with aldehydes without involving their free valence (reactions of this type are well known for *N*-oxide radicals[25]:



(In order to avoid the disproportionation of verdazyls under the influence of the hydrogen chloride liberated, the first reaction is carried out in the presence of triethylamine.) Bifunctional acyl chlorides or aldehydes give rise to verdazyl biradicals:


(X) (XI) (XII)

Aldose formazans have been used to synthesise water-soluble verdazyls[26]:


XIII

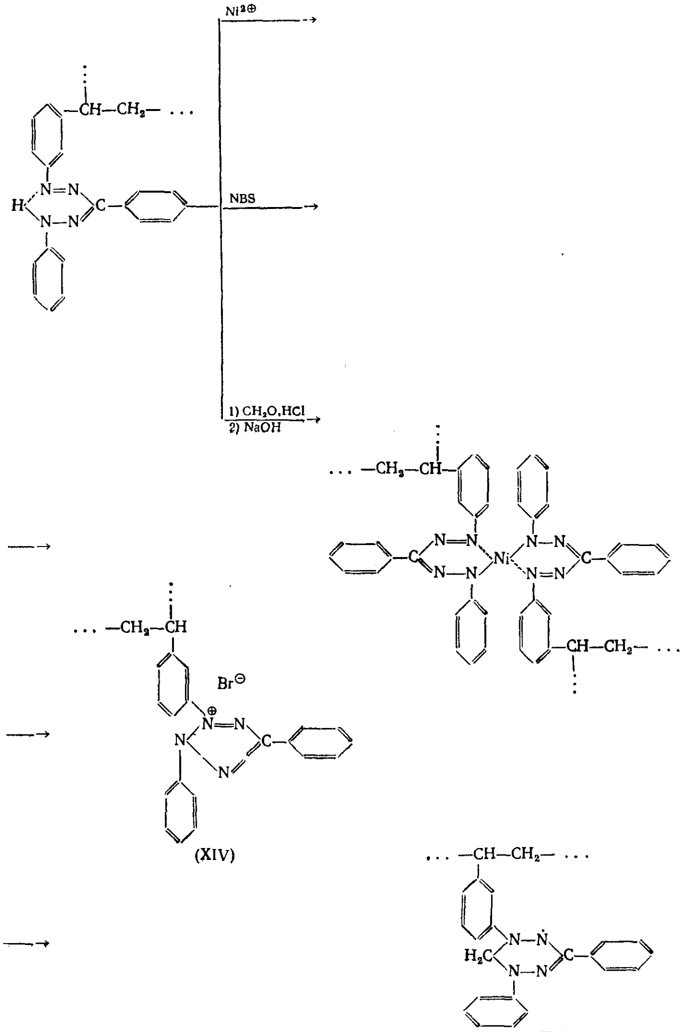
where R = D-*galacto*pentahydroxypentyl, D-*gluco*pentahydroxypentyl, D-*manno*pentahydroxypentyl, L-*rhamno*tetrahydroxypentyl, D-*arabino*tetrahydroxybutyl, or D-*xylo*tetrahydroxybutyl.

The photochemical formation of triphenylformazan on irradiation of (I),[2] on oxidation of (I) with atmospheric oxygen in the presence of activated charcoal[27], and when 3-aminoverdazyls are acted upon by acids and alkalis[9] constitutes chemical proof of the retention in verdazyl of the order of atoms in the initial formazan chain.

After long heating (at 80°C), (I) decomposes with formation of leucoverdazyl and 5-anilino-1,3-diphenyl-1,2,4-triazole in 1 : 1 proportions[28]. On thermal decomposition of (I) (at 200°C), aniline is formed in addition to these products[2]. Photochemical irradiation of (I) yields aniline, leucoverdazyl, and 1,3-diphenyl-1,2,4-triazole[29].

Formazans containing heteroaromatic substituents in the 1-, 5-, or 3-positions tend to undergo amine–imine tautomerism[30]. Formazans in which the heterocycle is not involved in tautomerism are most suitable for the synthesis of verdazyls[30-35].

Polymeric verdazyls and oligomers containing verdazyls in a polymer matrix are obtained by alkylating formazans or substituting them, by the anionic polymerisation of vinyl- and methacryloyl-verdazyls, and by the substitution of diaminoverdazyls with terephthalic aldehyde, terephthalic acid chloride, or styrene–maleic anhydride copolymers[36-45]. Polyurea containing verdazyls in the main chain has been obtained by the polyaddition of diverdazyldiamine and phenyl di-isocyanate[39]. Polycondensation of bisformazan with *p*-phenylenedimethylene dibromide yielded oligomers containing verdazyls[36]. A polymeric chelate, a polyverdazyl, and a polytetrazolium salt (a polymeric redox indicator) have been obtained by the polymerisation of polyvinylformazan[38]†:



(XIV)

(XV)

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† Here NBS = *N*-bromosuccinimide.

III. STRUCTURE AND SPECTRA

The geometry of the verdazyl skeleton was established by X-ray diffraction[46-49]. The heterocyclic verdazyl ring has the shape of an asymmetric boat with four coplanar nitrogen atoms and the $C_{(3)}$ and $C_{(6)}$ atoms at distances of 0.590 and 0.099 Å from the plane of the nitrogen atoms. The verdazyl heterocycle has a structure close to that of the planar *sym*-tetrazine and 3,6-diphenyl-*sym*-tetrazine[50,51]. The verdazyl ring contains N and C atoms of different valence, which leads to differences between the C–N distances in different parts of the ring (1.443 Å in the saturated component and 1.338 Å in the aromatic component). Fig. 1 presents the bond lengths and angles in radical (I) obtained by the X-ray diffraction analysis of a single crystal. The benzene rings at the $N_{(2)}$ and $N_{(4)}$ atoms are somewhat deformed owing to intermolecular forces and the planes of the rings deviate from the plane of the nitrogen atoms by 9° and 12°. The $N_{(1)}C_{(6)}N_{(5)}$ angle is close to the trigonal value, as a result of which the structure of the radical is favourable for the delocalisation of the unpaired electron. The benzene rings at the $N_{(2)}$, $N_{(4)}$, and $C_{(6)}$ atoms are also rotated relative to the $N_{(2)}$–CAr, $N_{(4)}$–CAr, and $C_{(2)}$–CAr bonds by 23°, 13.1°, and 1.6°. The appreciable dipole moment of (I) (2.94 D in benzene)[2] shows that the radical has a non-planar configuration in solution.

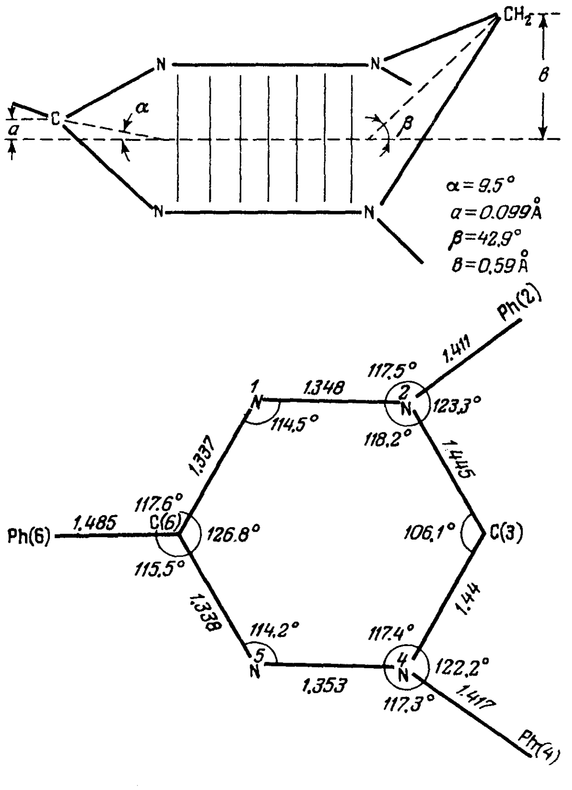


Figure 1. The bonds length and angles in the 2,4,6-triphenylverdazyl radical[46,47].

The electronic structures of verdazyls and the bond orders have been calculated by the simple and extended Hückel method[52-55] and also by the self-consistent field method in terms of the INDO approximation[56]. Calculation of ρ^{π} in radical (I) and in 2,4-diphenyltetrahydro-*sym*-tetrazinyl (XVI) by the Hückel method showed that the unpaired electron is localised mainly at the nitrogen atoms, where the spin densities are approximately the same (Fig. 2). The spin densities at the nitrogen atoms in the bi- and tri-radicals differ little from those in monoverdazyls[52].

We carried out a quantum-chemical calculation on the heterocycle in verdazyls by the unrestricted Hartree-Fock method in terms of the INDO approximation with complete optimisation of the geometry on the basis of a program employing a gradient method to find the proton energy minimum[216]. Fig. 3 presents the optimised bond lengths and angles in the boat conformer of a model verdazyl radical (the benzene rings have been replaced by hydrogen atoms). The calculations made it possible to explain satisfactorily the dipole moment found for triphenylverdazyl and the spectroscopic equivalence of the four nitrogen atoms of the verdazyl ring.

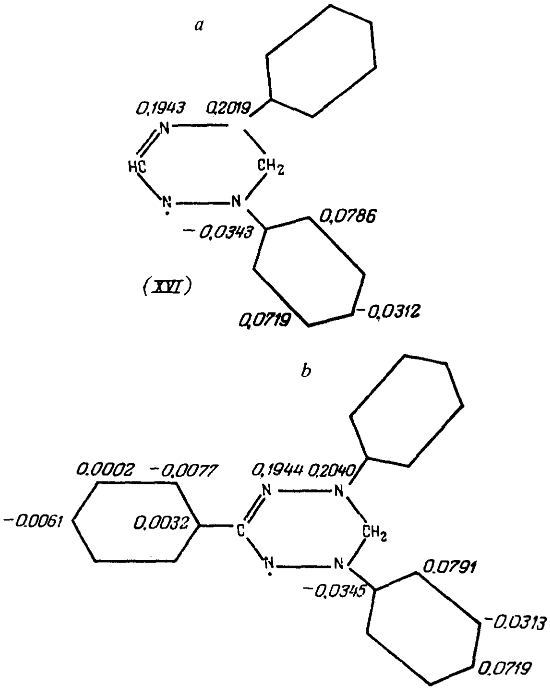


Figure 2. Distribution of spin densities: *a*) in the diphenylverdazyl radical (XVI); *b*) in the triphenylverdazyl radical[52].

The EPR spectrum of radical (I) consists of nine broad lines with a binomial intensity distribution (1 : 4 : 10 : 16 : 19 : 16...), which is due to the interaction of the unpaired electron with the four equivalent nitrogen atoms of the verdazyl ring[2,57]. The hyperfine interaction (HFI) constant $a^{N} \simeq 6$ G and the *g*-factor is 2.0033–2.0036.

The introduction of substituents in the *o*- and *p*-positions in the benzene rings of (IV) leads to the non-equivalence of the nitrogen atoms in pairs; the dependence of $a^{N}_{2,4}$ on the properties of the substituents then obeys the Hammett equation, while the constants $a^{N}_{1,5}$ are virtually independent of the nature of the substituent[22]. Arylverdazyls into which F, Cl, D, and Br atoms have been introduced selectively give rise to well resolved EPR spectra at room temperature. Splittings are observed due to protons in the equivalent benzene rings attached to the $N_{(2)}$ and $N_{(4)}$ atoms: $a^{H}_{o} = a^{H}_{p} = 1.06-1.09$ G; $a^{H}_{m} = 0.41-0.49$ G.[15]

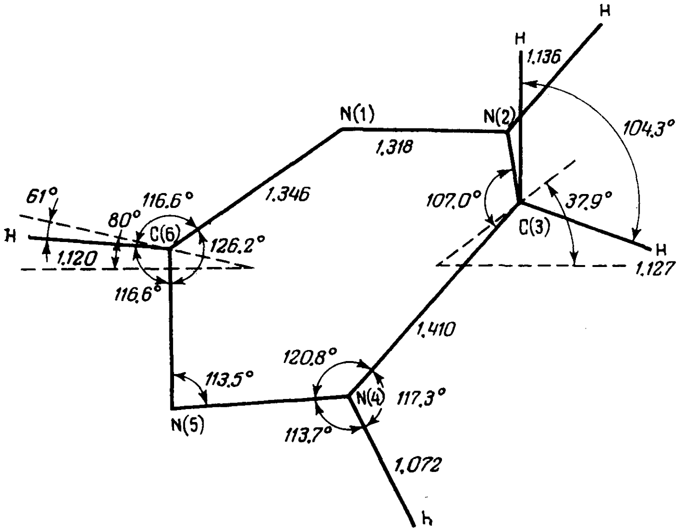
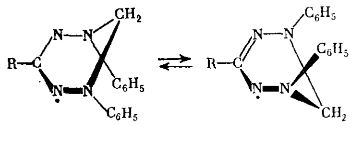


Figure 3. The steric structure of a model verdazyl radical[216].

The paramagnetic shifts relative to diamagnetic leucoverdazyls have been determined from the NMR spectra for many verdazyl radicals with aliphatic substituents and the isotropic HFI constants have been found[10,53,58–61]. The HFI constants (in G) have been obtained from the NMR spectra of (I) in $CDCl_3$ for all its protons[53]: for the protons of the benzene rings attached to $N_{(2)}$ and $N_{(4)}$ ($a^{H}_{p} = 1.195$, $a^{H}_{o} = 1.12$, $a^{H}_{m} = 0.425$), for the protons of the $C_{(6)}$–benzene ring ($a^{H}_{p} = 0.31$, $a^{H}_{o} = 0.425$, $a^{H}_{m} = 0.16$), and for the $C_{(3)}$-methylene protons ($a^{H} = 0.027$)[53]. The electronic-nuclear double resonance (ENDOR) spectra of dilute liquid solutions of verdazyls have been investigated[62]; the constants for the hyperfine interaction with the protons in the *o*-, *m*-, and *p*-positions in the aromatic rings agree with the values measured previously by EPR and NMR (Table 1). The signs and values of the HFI constants found by the NMR method agree with the spin densities calculated from the experimental data using the McConnel and Stone–Maki equations[15,53], and with the spin densities obtained by the Hückel and McLachlan quantum-chemical calculations[52]. The constant for the hyperfine interaction with the protons of the CH_2 group in the 3-position of the verdazyl ring is positive for all the monoverdazyls and amounts to 0.027–0.031 G.[15,58,62] The temperature dependence of the NMR spectrum of this group indicates the inversion of the verdazyl ring[10,60]:



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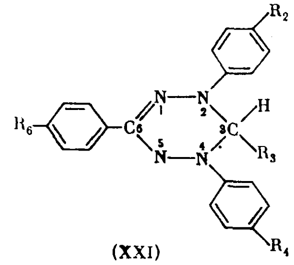
Hyperfine interaction with protons located at large distances from the point at which the initial spin density is localised (separated by 3–4 σ bonds) has been observed for verdazyls with aliphatic substituents in the 3- or 6-positions and in the *p*-positions in the *N*-phenyl rings (Table 2). The characteristics of the distribution of spin density in verdazyl σ systems depend on the geometrical structure of the radicals[53,58–61].

Table 1. The hyperfine splitting constants of verdazyls (G) measured by the ENDOR method[62].



(XXI)

a) $R_2 = R_3 = R_4 = R_6 = H$;
b) $R_2 = R_3 = R_4 = H$; $R_6 = CH_3$;
c) $R_2 = R_4 = CH_3$; $R_3 = R_6 = H$;
d) $R_2 = R_4 = R_6 = CH_3$; $R_3 = H$;
e) $R_2 = R_4 = R_6 = H$; $R_3 = CH_3$

Radical	a^{*N}	$a^{H}_{2,4\text{-p}}$	$a^{H}_{2,4\text{-}o}$	$a^{H}_{2,4\text{-m}}$, $a^{H}_{6\text{-}o}$	$a^{CH_3}_{6\text{-p}}$	$a^{CH_3}_{3}$
(XXIa)	5.79	1.22	1.11	0.42	—	—
(XXIb)	5.67	1.28	1.11	0.42	0.30	—
(XXic)	5.75	1.29	1.12	0.41	—	—
XXId)	5.62	1.29	1.12	0.41	0.30	—
(XXIe)	5.60	1.26	1.15	0.42	—	0.97

* According to EPR data in 2-methyltetrahydrofuran.

^{19}F dynamic nuclear polarisation (DNP) has been investigated in solution in the presence of verdazyls. The heterocyclic group of verdazyls has a high spin density and readily forms complexes with C_6F_6, the contact interaction making a significant contribution to the polarisation[63,64].

The EPR spectra of the polymers based on verdazyl radicals are non-characteristic and usually consist of a single or several broadened lines[37,38,65].

The EPR spectra of verdazyl bi- and tri-radicals[20,21,24] are less well resolved than those of the monoradicals, which is primarily due to the electron–electron interaction‡. A detailed study of the verdazyl biradicals (V) and (VI) by EPR and NMR showed that the constant for the

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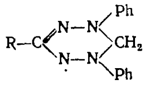
‡ An increase in molecular size can also lead to an impairment of the averaging of the anisotropic HFI.

hyperfine interactions with the protons of the aromatic rings joining the verdazyl moieties are equal to the average HFI constants for the corresponding protons in monoverdazyl, while the temperature dependence of the paramagnetic shifts is linear. Hence it follows that the exchange energy in the verdazyl biradicals obeys the relation $RT > J > a^N$. In the spectra of radicals (XI) with $n = 0$ splitting by the eight equivalent nitrogen atoms is observed ($a^N = 2.9$ G) but, when $n = 6$, the usual spectrum of verdazyl monoradical is observed (four N atoms, $a^N = 5.8$ G). The exchange interaction energy J then changes from $J > 6$ G ($n = 0$) to $J \simeq 0$ ($n = 6$).[24] In dilute solid solutions of verdazyl bi- and tri-radicals, dipole splitting is observed. The dipole interaction constants D of the electrons in verdazyl biradicals are 10–55 Oe, depending on the structure[66–69]. The values of D for (V) and (VI) are respectively 43.1 and 52.7 G, whence the average distances between the paramagnetic centres (8.7 and 8.1 Å) were found.

Table 2. The isotropic constants (G) for the hyperfine interaction with protons in the 3-position in verdazyls*[60].



R	a_{H_α}	a_{H_β}	a_{H_γ}	a_{H_δ}
H	0.72	—	—	—
CH_3	—	−2.03	—	—
$C(CH_3)_3$	—	—	0.105	—
CH_2CH_3	—	−1.63	0.168	—
$CH(CH_3)_2$	—	−1.17	0.120	—
$CH_2C_6H_5$	—	−1.34	—	—
$CHCH_3C_6H_5$	—	−1.04	0.124	—
$CH_2CH(CH_3)_2$	—	−1.50	0.275	0.038
$CH_2CHCH_3C_2H_5$	—	−1.63; −1.41	0.260	—
$CH_2CHCH_3C_6H_5$	—	−1.57; −1.41	0.282	0.037
$CH{=}CHC_6H_5$	—	−0.953	0.832	

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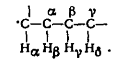
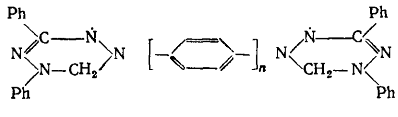
* The positions of the atoms relative to the radical centre are as follows:



The study of EPR spectra and magnetic susceptibility over a wide temperature range showed that radicals (VIII) ($n = 4$) and (V) are biradicals with a virtually degenerate singlet–triplet ground state, while triradical (VII) has a virtually degenerate doublet–quartet ground state[6,67]. Biradicals (IX) and (XVII),



(XVII) $n = 2, 3, 4,$

exhibit a decrease of paramagnetism on reducing the temperature, which is believed[21] to be a result of equilibrium with the corresponding diamagnetic zwitter-ionic forms.

In order to study diverdazyl radicals in frozen solid solutions (toluene or polystyrene matrices at 77 K), two- and three-pulse EPR spectroscopy has also been used[70]. Transitions from the triplet level (for which $\Delta M = 1$) are then observed.

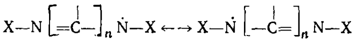
In order to find the parameters of the g-tensor and the tensor of the HFI constants, a study was made of the EPR spectra of radical (I) in a 2,4,6-triphenylbenzene diamagnetic single crystal matrix[71]. When the single crystal is rotated in a magnetic field, the EPR spectrum changes and additional splitting (seven lines), attributed to radical pairs and three-membered radical clusters, is observed. Studies of this kind are of interest from the standpoint of using verdazyls as paramagnetic probes in studies on molecular mobility in crystals and phase transitions.

Like other stable radicals, verdazyls catalyse the ortho-para conversion of hydrogen; the catalytic property depends strongly on the magnetic moment and structure of the verdazyl[72–74].

The characteristics of the behaviour of magnetic susceptibility in crystalline verdazyl radicals, determined by the exchange interaction of the electrons, have been studied[21,48,49,75,76]. The magnetic susceptibility of verdazyls obeys the Curie–Weiss law with negative θ constants [$\theta = -14.6$ K for (I)], over a wide temperature range (300–30 K). However, below 30 K the curves for the temperature dependence of this susceptibility have maxima indicating the occurrence of antiferromagnetic interactions [at 6.9 K for (I) and at 12 K for (III)]. At temperatures below $T_{\max}$ the EPR lines are broadened and the g-factor shifts, which indicates the occurrence of magnetic phase transitions. The magnetic properties of the radicals are extremely sensitive to the distribution of the unpaired electron and to the way in which the molecules are packed in the crystal. The different magnetic properties of (I) and substituted triarylverdazyls are associated mainly with the different types of molecular packing of the radicals. Azuma and coworkers[48,49] showed that verdazyls are linear spin systems and can serve as convenient model compounds for the investigation of ferromagnetic interactions in stable radicals.

The study of the frequency and temperature dependence of the EPR line width in the spectrum of (I) yielded information about the exchange and dipole–dipole interactions[77]. The EPR line width for (I) is independent of frequency and temperature (in the range 300–100 K) and approaches the limit corresponding to maximum narrowing. The spin exchange frequency (111 GHz) and the upper limit for the dipole interaction ($D = 288$ G) have been estimated[77]. The high spin exchange frequency is associated with the strong intermolecular overlapping of the $2p\sigma$ and $2p\pi$ orbitals of the aromatic rings of the verdazyl radical in the solid state.

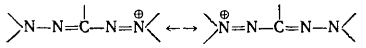
According to Dahne[78], verdazyls are electrically neutral polymethine cyanines having the general formula



$$X{-}N\left[\overset{|}{=}C{-}\right]_n\ddot{N}{-}X \longleftrightarrow X{-}\ddot{N}\left[{-}\overset{|}{C}{=}\right]_n N{-}X$$

where the CH_2 bridge links the ends of the cyanine chain in the *cis-cis* positions with formation of a six-membered ring. Monoverdazyls[2,9,22,79] as well as verdazyl bi-, tri-, and poly-radicals[21,36–45] absorb in the visible region of the spectrum (at 400 and 700 nm). In polar solvents the bands undergo a bathochromic shift which makes it possible to assign them to $\pi \to \pi^*$ transitions[29]. A bathochromic shift of both bands has been observed for triarylverdazyls with electron-donating or electron-accepting substituents, because this entails an increase in the conjugation system, which stabilises the first excited state to a greater extent than the ground state and thus reduces the excitation energy regardless of the nature of the substituent[22]. The substituent in the 3-position, which is not involved in the conjugation system, causes a small hypsochromic shift (20–30 nm) of the long-wavelength absorption band. For the colourless leucoverdazyls substituted in the *p*-position of the $C_{(6)}$-phenyl ring, the shift of the long-wavelength absorption band maximum (~330 nm) is satisfactorily correlated with the Hammett σ constants for the substituents[80].

Verdazyl cations are regarded as azacyanine cations having the general formula



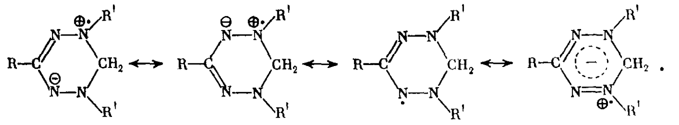
$$>N-N=\overset{|}{C}-N=\overset{\oplus}{N}< \longleftrightarrow >\overset{\oplus}{N}=N-\overset{|}{C}=N-N<$$

in which two $-CR=$ groups have been replaced by $-N=$.[22,78] The introduction of substituents in the $C_{(6)}$-ring of triarylverdazyl cations leads to a bathochromic shift of λ_{max} in the presence of electron-donating substituents and to a small hypsochromic shift in the presence of electron-accepting substituents[22,79,81]: NO_2 (535 nm), Cl (545 nm), H (548 nm), CH_3 (553 nm), and OCH_3 (576 nm). Solutions of verdazyl radicals, cations, and leuco-bases obey the Beer–Lambert law. The monomeric state of verdazyl radicals in solutions has also been demonstrated by EPR.[82] Quantum-chemical calculations (LCAO-MO and SCF LCAO-MO in terms of the INDO approximation)[52–56] do not provide an interpretation of the electronic absorption spectra of verdazyls.

The infrared spectra of verdazyls and their cations and leuco-bases have been studied in detail[2,54,55,83–86]. The similarity of the atomic weights of carbon and nitrogen leads to a strong interaction of the vibrations, so that the interpretation of the spectral lines in terms of the vibrations of individual bonds is not sufficiently rigorous[54]. When the ^{15}N label is introduced into (I) all the bands in the infrared spectrum are displaced towards longer wavelengths compared with the species containing ^{14}N, which indicates the presence of a conjugation chain in the verdazyl system[6]. The infrared spectra of the leuco-bases showed the characteristic bands of the N–H bonds (~3300 cm^{-1}). The bands in the region of 1600 cm^{-1} have been assigned to the vibrations of the $C_{(6)}=N_{(5)}$ bond; in triphenylverdazyl and its leuco-base it is intense, while in the cations it is weaker (these bands, which are superimposed on the vibration bands of benzene rings, become resolved in the presence of the ^{15}N label[6]). The 1155–1165 cm^{-1} band, assigned to the $-N=N-$ stretching vibrations, characterises the distribution of electron density in the ring. The spectrum of (I) shows in this region a doublet at 1122–1165 cm^{-1}, which is absent from the spectra of the leuco-bases. The intense 1260 cm^{-1} band, assigned to the $N_{(5)}-C_{(6)}-N_{(1)}$ bond[54,55,83–86], is observed for verdazyl radicals and cations but not for the leuco-forms. It is located at a higher level than in the spectra of formazans having the symmetrical $N_{(2)}-C_{(3)}-N_{(4)}$ linkage[87]. The infrared spectra of verdazyls in general confirm a symmetrical distribution of the unpaired electron.

IV. CHEMICAL PROPERTIES

Verdazyls belong to the class of the most stable free radicals. Crystalline (I) remains unchanged for many years. This is due to the strong delocalisation of the unpaired electron, which lowers the energy of the ground state of the radical, and to the steric shielding of the verdazyl ring. It can also be accounted for on the basis of the principle of the "merostabilisation" of free radicals[88]:



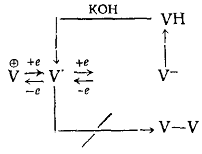
The stability of verdazyls is to a large extent determined by the ability of the 6-substituent in the 6-position to cause the steric stabilisation of the verdazyl ring[6] and varies in the sequence[2,10,15,57,89]

$$RS < H < CH_3 < COOR < C(CH_3)_3 < C_6H_5.$$

The introduction of alkyl or phenyl substituents in the 3-position increases the stability of the verdazyl radical[6,27]. Leucoverdazyls are readily dehydrogenated by other stable radicals—DPPH and tri-t-butylphenoxyl[90]. In the reaction with 2,2,6,6-tetramethylpiperidin-1-yloxy-radical the equilibrium is displaced towards (I). Thus the stability of triarylverdazyls greatly exceeds that of phenoxy- and hydrazyl radicals and is not inferior to that of the ultrastable iminoxy-radicals.

1. Electrochemical Reactions

The polarographic oxidation-reduction of substituted triarylverdazyl radicals ($V^{\cdot}$) in solution in DMF, CH_3CN, and propylene carbonate (PC) at a dropping mercury electrode takes place reversibly with transfer of one electron and may be described schematically as follows[91–93]:

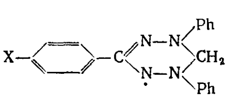


The half-wave oxidation and reduction potentials ($E_{1/2}$) for (II) depend on the nature of the substituents (Table 3). As was to be expected, as the electron-donating properties become more pronounced, the oxidation-reduction half-wave potential shifts towards lower values. The effect of the substituent is described satisfactorily by the modified Hammett–Zuman equation: $\Delta E_{1/2} = E^{X}_{1/2} - E^{0}_{1/2} = \rho_{\pi}\sigma$. The reaction constants characterising the polarisability of the electrochemically active group depend little on the nature of the solvent (Table 4). However, in methanol ρ_{π} for the reduction reaction changes sign, which indicates an electrophilic mechanism. It appears that the kinetics of the protonation in the electrode field preceding electron transfer play a decisive role in the reduction[94]. Comparison of the oxidation-reduction half-wave potentials of (I) and the water-soluble verdazyl (XIII) (R = D-*galacto*-pentahydroxypentyl), whose molecules are capable of forming an intramolecular hydrogen bond, shows that the oxidation half-wave potentials in various solvents differ little (within the limits of the differences between the potential of the liquid compound and the value in solvents and water)[94]. However, there is a difference between the reduction half-wave potentials of (I) and (XIII). The formation of an intramolecular hydrogen bond is accompanied by a small change in $E_{1/2}$ (intramolecular protonation). Thus, when (XIII) is transferred from CH_3CN to CH_3OH, $E_{1/2}$ increases by 0.08 V, while the corresponding increase for (I) is by 0.51 V,[91,94] the reduction half-wave potentials of triarylverdazyls depending to a greater extent on the specific solvation effects than on the substituent effects. This is apparently associated with the involvement of mobile hydrogen atoms of alcohols in the potential-determing stage of the electrode process. Indeed the reduction half-wave potentials of (I) and (XIII) vary in parallel with pK_a for the autoprotolysis of the organic solvents[91,94]. These data demonstrate the importance of taking into account the proton transfer reactions when the reactivities of verdazyls are considered.

Comparison of electrochemical data for stable radicals makes it possible to estimate qualitatively their donor–acceptor properties. The radicals can be arranged in the following activity series in terms of their reducing capacity: perchlorodiphenylmethyl[95], tri-t-butylphenoxyl[96], DPPH,[97] di-t-butylnitroxide[98], *N*-oxides[99], triphenylmethyl[100], triphenylverdazyl[91].

In this series the most powerful electron donor is the triphenylverdazyl radical, which must be regarded as a Lewis base. Thus chlorinated triphenylmethyl radicals are virtually inert with respect to powerful electrophiles such as the halogens and concentrated nitric acid[5,101], phenoxyls are oxidised only under the influence of powerful oxidants ($SbCl_5$ and other metal halides)[102], while (I) or triphenylmethyl radicals react almost instantaneously with halogens to form cations[2,101].

Table 3. The half-wave potentials for the polarographic oxidation-reduction of triarylverdazyls in propylene carbonate and methanol at 25°C.[21,93]



X	Reduction		Oxidation		X	Reduction		Oxidation	
	angular coefficient, mV	$E_{1/2}$, V	angular coefficient, mV	$E_{1/2}$, V		angular coefficient, mV	$E_{1/2}$, V	angular coefficient, mV	$E_{1/2}$, V
	Propylene carbonate					Methanol			
NO_2	65	—0.68	65	0.305	NO_2	90	—0.300	55	0.250
Cl	60	—0.72	60	0.235	CO_2CH_3	90	—0.270	65	0.190
CO_2CH_3	70	—0.71	65	0.240	Cl	90	—0.275	65	0.180
H	60	—0.725	70	0.200	H	90	—0.270	65	0.160
CH_3O	70	—0.755	75	0.165	CH_3O	90	—0.250	60	0.120
CH_3O*	80	—0.770	75	0.110	CH_3O *	90	—0.250	65	0.070

* 2,6-Bis-(4-methoxyphenyl)-4-phenylverdazyl.

2. One-Electron Transfer Reactions

One-electron transfer reactions play an important role in the mechanisms of the elementary steps of many organic and bio-organic reactions[103]. Model reactions involving triphenylverdazyls and their salts, in which the one-electron transfer stage has been clearly detected by physicochemical methods, are discussed below. Verdazyls are some of the most powerful nucleophiles and in their reactions with electrophiles give up an electron and are converted into stable cations. Such reactions include those of (I) with halogens[2,104], Lewis acids[2,21,79,105-107], and various inorganic oxidants[2,108]. When a green solution of (I) is mixed with oxidants, a violet verdazyl salt is formed instantaneously. The stability of the diamagnetic cation depends on the nature of the substituent in the radical, the nature of the oxidant and the medium, and other conditions.

Table 4. Correlation equations for chemical reactions involving verdazyls.

X-R*	Reaction of substrate	*T*, °C	Solvent	Reaction constants (parameters of the substituents with which they are correlated)	Corresponding correlation coefficient	Isokinetic temp.**	Refs.
X—R	electrochemical oxidation	25	DMF	1.99 (σ)	0.990	—	91
X—R	ditto	25	CH_3OH	2.02 (σ)	0.992	—	91
X—R	electrochemical reduction	25	DMF	1.36 (σ)	0.995	—	91
X—R	ditto	25	CH_3OH	—0.71 (σ)	0.936	—	91
X—R	$ClCH_2CO_2H$	20	C_2H_5OH	—3.13 (σ), —23.42 ($E_{1/2}$), —0.81 (pK_a)	0.993; 0.989; 0.989	—	90
X—R	ditto	20	DMF	—2.17 (σ), —16.74 ($E_{1/2}$)	0.994, 0.997	—	90
X—R	PhSH	20	CH_3CN	—0.90 (σ), —8.65 ($E_{1/2}$)	0.999, 0.987	363	90
X—R	$C(NO_2)_4$	20	C_6H_{12}	—2.17 (σ), —20.8 ($E_{1/2}$)	0.999, 0.981	—	107
X—R	ditto	20	THF	—1.13 (σ), —11.0 ($E_{1/2}$)	0.994, 0.985	—	107
X—R	HB	25	DMF	—0.31 (σ), —0.23 ($σ^+$), —2.51 ($E_{1/2}$)	0.977; 0.992; 0.970	—	147
X—R	ditto	25	C_2H_5OH	—0.42 (σ), —0.31 ($σ^+$), —3.54 ($E_{1/2}$)	0.983; 0.995; 0.992	—	147
X—R	BDN	25	DMF	0.23 (σ), 2.96 ($E_{1/2}$)	0.990, 0.991	335	90, 129
X—R	HE	25	DMF	0.14 (σ), 1.81 ($E_{1/2}$)	0.994, 0.988	—	90, 129
X—R	BDN	25	C_2H_5OH	—0.16 ($σ^+$), 4.81 ($E_{1/2}$)	0.967, 0.960	—	90, 129
X—R	HE	25	C_2H_5OH	—0.40 ($σ^+$), 12.36 ($E_{1/2}$)	0.976, 0.963	—	90, 129
X—R	$(C_6H_5CO_2)_2$	20	propylene carbonate	—0.35 (σ), —2.81 ($E_{1/2}$)	0.995, 0.997	370	125
H—R	$(p\text{-}XC_6H_4CO_2)_2$	20	ditto	1.17 ($σ^\circ$), 32.87 ($E_{1/2}$)	0.993, 0.981	—	167
H—R	ditto	20	C_6H_6	1.22 ($σ^\circ$), 34.15 ($E_{1/2}$)	0.995, 0.984	—	167
X—R+	$C_6H_5NHC_2H_5$	20	CH_3CN	0.37 (σ)	0.976	—	81
H—R+	$p\text{-}XC_6H_4NH_2$	20	ditto	—5.01 (σ), —5.75 ($E_{1/2}$), 1.86 (pK)	0.967; 0.987; 0.960	—	81
X—R+	HB	20	"	0.97 (σ), 9.38 ($E_{1/2}$)	0.993, 0.992	—	162
H—R+	X-HE***	20	"	—1.21 (σ), —4.82 ($E_{1/2}$)	0.995, 0.953	528	164

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* Triarylverdazyl radicals (X–R) and their salts $(X\text{–}R)^+$ substituted in the *p*-position of the $C_{(6)}$-phenyl ring.

** The average isokinetic temperature determined by various methods (from the relation between E_a, on the one hand, and $\Delta S^{\neq}$, $\lg k_{2,T_1}$, and $\lg k_{2,T_2}$, on the other, and between ρ and $1/T$, etc.).

*** 3,5-Diethoxycarbonyl-2,6-dimethyl-4(X)-1,4-dihydropyridines.

The influence of the nature of the substituent in (II) and of the polarity of the medium on the kinetics and mechanism of the reaction

$$\dot{V} + C(NO_2)_4 \begin{cases} \longrightarrow \overset{\oplus\ominus}{VC}(NO_2)_3 + N\dot{O}_2 & \text{(non-polar solvents),} \\ \longrightarrow \overset{\oplus\ominus}{VC}(NO_2)_3 + \overset{\oplus\ominus}{VNO_2} & \text{(polar solvents)} \end{cases}$$

has been studied[107] in relation to the model reaction involving electron transfer from triarylverdazyl to tetranitromethane (TNM). In polar solvents radicals (II) react with $NO_2^{\cdot}$ in a solvent cage {the stoichiometry corresponds to $[(II)]/[TNM] > 1$}. The reaction is characterised by relatively small activation parameters E_a = 3–5 kcal mole^{-1} and $\Delta S^{\neq}$ = –35–20 e.u. The rate of reaction $v = k_2[V^{\cdot}][TNM]$ depends significantly on the polarity and solvating capacity of the solvent (on passing from cyclohexane to propylene carbonate, k_2 increases by a factor greater than 10^3). The effect of the substituent in the *p*-position relative to the $C_{(6)}$ -phenyl ring of (II) can be described satisfactorily in terms of the Hammett equation (Table 4). The solvation of (II) by tetrahydrofuran molecules[109] leads to an appreciable decrease of the influence of the polar properties of substituents (Table 4). The rates of reaction of (II) with TNM are also satisfactorily correlated with the polarographic oxidation potentials of (II) (Dimroth's equation) (Table 4). This type of relation between the kinetic and thermodynamic parameters of the reaction with high proportionality coefficients is regarded as evidence for electron transfer in the rate-determining stage[110].

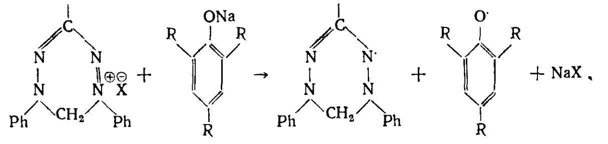
When (I) interacts with tetracyanoethylene and chloranil, which gives rise to stable radical-anions on reduction, the EPR spectra of (I) and the oxidant radical-anion are superimposed, the intensity of the former decreasing with time and that of the latter increasing; the electronic spectra show clearly the absorption band due to the verdazyl salt[108,111]. When the difference between the donor–acceptor properties of the free radicals is fairly large, their interaction may occur via the transfer of one electron and may lead to the formation of a corresponding cation and anion. We observed this in the reaction of (II) with acyloxy-radicals formed in the decomposition of diacyl peroxides[112,113] ($PhCOO^{\cdot}$, $C_6H_{13}COO^{\cdot}$, $C_{11}H_{23}COO^{\cdot}$), NO_2,[107] and acetyl radicals formed in decomposition of lead tetraacetate[108]. Radical (I) recombines with active radicals such as $^{\cdot}CH_2Ph$, $(CH_3)_2\dot{C}COCH_3$, radicals derived from monomers[114-117], $(CH_3)_2\dot{C}CN$,[118], and $^{\cdot}CH_3$,[119] forming addition products (tetrazines). Such recombination makes it possible to classify $^{\cdot}CH_3$ and 1-cyano-1-methylethyl radicals as nucleophiles, which agrees with the view of Ingold and Roberts[120]—halogen-containing free radicals and the majority of radicals with the free electron centred on O or S atoms are classified by these workers as electrophiles, while triethylstannyl, methyl, cyclohexyl, and 1-cyano-1-ethyl radicals are classified as nucleophiles.

In 1973 we attempted[93] to carry out a similar classification for stable radicals and discussed the problem of one-electron transfer in a pair of verdazyl radicals differing greatly in their donor–acceptor properties.

Verdazyls do not react with trityl radicals (but they do react with Ph_3COO), DPPH, and the 2,2,6,6-tetramethyl-4-oxopiperidin-1-yloxy-radical, apparently owing to the presence of bulky substituents in the region of the reaction centres[65,116]. However, (I) reacts with phenoxy-radicals via one-electron transfer with the formation of the corresponding salt[108,111,121,122]. The rate of reaction of substituted phenoxy-radicals with (I) increases with increase of the electron-accepting capacity of the substituent in the *p*-position of the benzene ring, with decrease of $E_{1/2}$ for the polarographic reduction of phenoxy-radicals, and with increase of electron density in the *p*-position of the phenoxy-radical[111].

Like verdazyl monoradicals, the biradicals are readily oxidised by Lewis acids and peroxy-compounds, being converted into diamagnetic salts. It has been shown[123] that the polarographic oxidation of (VI) is reversible, with successive transfer of two electrons. Presumably the oxidation of verdazyl biradicals by strong oxidants also takes place via consecutive one-electron transfer.

In contrast to the radicals, verdazyl salts exhibit pronounced electron-accepting properties. One-electron reduction of verdazyl salts is one of their characteristic reactions and, in view of the high stability of verdazyls, the reaction frequently stops at this stage. Verdazyl salts are used as electrophilic components in order to confirm the hypothesis of one-electron transfer in the interaction of two diamagnetic substances (reactions with tetramethyl-*p*-phenylenediamine and with sodium tri-t-butylphenoxide)[79,108,124]



R = t-butyl.

The resulting EPR spectrum corresponds to the superposition of the spectra of two radicals: (I) and tri-t-butylphenoxyl. When verdazyl salts interact with leucoverdazyls, two verdazyl radicals are also formed[79,90]. If metallic potassium or sodium, an alkali metal alkoxide, or an alkali metal phenoxide is used as the donor, the reaction with verdazyl salts proceeds almost instantaneously[108]. In the reaction with alcohols the verdazyl salt is reduced to the initial radical (methanol is then oxidised to formaldehyde)[125].

Reactions involving one-electron transfer to verdazyl salts occur readily when aromatic and aliphatic amines are used as the donors[81,124,126,127]. The rate of oxidation of amines by verdazyl salts is almost independent of the nature of the salt counterion and of the replacement of H by D in the amino-group[126]. The activity of amines is determined by both electronic and steric effects; they depend to a large extent on the nucleophilic properties of the amine. On passing to aliphatic amines[127], the rate of oxidation of verdazyl salts increases by 2–4 orders of magnitude compared with aromatic amines due to the decrease of E_a (aliphatic amines are much stronger nucleophiles). It is noteworthy that in the reactions with amines the yield of radical (II) is approximately 70–80% for $PhNR'_2$ and aliphatic amines, approximately 60–70% for $PhNR'H$, and approximately 10–15% for $PhNH_2$ (this is apparently due to side reactions of verdazyl salts[2,18]). The amine radical-cation formed in the elementary electron transfer step readily splits off a proton and is converted into an amine radical, which then either reacts with (II) in the solvent cage or emerges from the latter, which entails the accumulation of (II). The rate of oxidation of anilines is relatively insensitive to the electronic effects of the substituent in the salt (Table 4). In the oxidation of *p*-substituted anilines by verdazyl salts Hammett's, Dimroth's, and Brønsted's correlation equations are found to hold (Table 4). The occurrence of such correlations shows that the mechanisms of all the reactions have a feature in common, believed nowadays to be one-electron oxidation-reduction (*SET* mechanism)[103,110].

The foregoing considerations show that verdazyl radicals may be used in chemistry as one-electron reductants, while verdazyl salts can be used as one-electron oxidants.

3. Reactions of Verdazyls with Acids

The majority of stable radicals react with protic acids; the possibility of such reactions is determined to a large extent by the nucleophilic properties of the radicals. This can explain the high stability of perfluorodimethylnitroxide, di-(4-nitrophenylaminoxyl), 3-imidazolinyl, and porphyrexide in relation to inorganic acids[128]. Being strong nucleophiles, verdazyls are readily oxidised by various acids and, depending on the proton-donating properties of the acid, there is a gradual transition from proton and electron transfer to homolytic substitution reactions[90].

The reaction of (II) with carboxylic acids involves the reversible formation of the cation and the verdazyl leuco-base[2]:

$$2V^{\cdot} + R'CO_2H \overset{K_p}{\rightleftarrows} VH + V^{+}R'COO^{\ominus}$$

The state of equilibrium in the acid-base interaction depends on the donor-acceptor properties of the reactants, their structure and concentration, the nature of the solvent, and temperature[90,129]. When (I) interacts with inorganic (H_2SO_4, HBr, HNO_3) and strong organic acids (CF_3CO_2H, CCl_3CO_2H), the equilibrium is greatly displaced towards the formation of the products, VH being oxidised to the radical and being thus gradually converted into a salt[2]. A study of the equilibrium between (II) and $ClCH_2CO_2H$ showed[130] that, depending on the nature of the solvent, the effective equilibrium constant depends on the concentration of the acid (in alcohol) or on its square (in DMF), or on the concentration of the acid dimer(in benzene), and, depending on the substituent in the *p*-position of the $C_{(6)}$-phenyl ring of (II), the equilibrium constant changes by several orders of magnitude[131,217]. In alcohol and DMF the equilibrium constants are satisfactorily correlated with Hammett's σ constants of the substituents and the polarographic oxidation potentials of verdazyls (Table 4). Verdazyls enter into this reaction as electron donors and the high coefficients in the correlation equations indicate an appreciable charge separation in the activated complex of the reaction. The solvent effect is associated mainly with the change in the proton-donating properties of the acid[129]. There is a linear relation between the disproportionation constants of (II) and the pKa of the acids (Brønsted's equation) (Table 4). Since the ionisation of acids reduces to proton transfer from the acid to the solvent and the reaction of HX with triarylverdazyls apparently involves partial proton transfer from HX to (II), it is clear that the free energies of the two processes are related. The proportionality coefficient in Brønsted's equations indicates the decisive role of proton transfer[132] in the reaction of (II) with protic acids.

The reaction of (II) with protic acids is believed to proceed via a series of consecutive equilibria[90,217]. The formation of hydrogen-bonded complexes (*a*), proton transfer via the hydrogen bond with formation of a close ion pair (*b*), the dissociation of ion pairs (*c*), electron transfer from the free verdazyl radical to the protonated radical (*d*), and protonation of the resulting leuco-base (*e*):

$$V^{\cdot} + HX \underset{a}{\rightleftarrows} V^{\cdot} \ldots HX \underset{b}{\rightleftarrows} VH^{\oplus\cdot} \ldots X^{\ominus} \underset{c}{\rightleftarrows} VH^{\oplus\cdot} + X^{\ominus} \underset{d}{\overset{V^{\cdot}}{\rightleftarrows}} VH + V^{\oplus}X^{\ominus} \underset{e}{\rightleftarrows} VH_2^{\oplus}X^{\ominus} + V^{\oplus}X^{\ominus}$$

The equilibrium constant for stage *b* depends on the strength of the acid HX and the base $VH^{\oplus}$ and can be estimated approximately in terms of the quantity $\Delta pK_a = pK_{VH^{\oplus}} - pK_{HX}$. The solvent participates in processes *a*–*e* as an active proton donor. Electron-accepting substituents in verdazyls reduce the basicity of both $V^{\cdot}$ and VH, the equilibria in processes *b*, *c*, and *d* being displaced to the left in the direction of the initial reactants. The thermodynamic parameters of the reaction of (II) with acids ($\Delta H^{\circ} = -2-5$ kcal mole^{-1}, $\Delta S^{\circ} = -5-20$ e.u.)[90,129] are consistent with the parameters of the proton transfer reaction in the interaction of amines with carboxylic acids. In DMF, chloroacetic acids apparently form 1 : 2 ion pair complexes i.e. $[VH^{\oplus}][HX(X^{\ominus})]$ [in the reaction of (II) with carboxylic acids the equilibrium in process *e* is apparently fully displaced to the left]. Comparison of the pK values for free radicals shows that verdazyls are the most basic species: p$K \simeq 1$ for triphenylphenoxyl, p$K = 5.5 \pm 2$ for 2,2,6,6-tetramethylpiperidin-1-yloxyl[133], and p$K \simeq 6.2$ for (XIII).[26]

An experimental study of the kinetics of the disproportionation of (II) in the presence of carboxylic acids showed[134] that the rate of reaction is determined by the stage involving electron transfer from free $V^{\cdot}$ to the solvated species: $v = k_3[V^{\cdot}]^2[R'CO_2H]$. The reaction with hydrogen halides may be used for the potentiometric determination of verdazyl[65]. The use of triarylverdazyls in the study of the kinetics of the ionisation of t-butyl halides in organic solvents is based on this factor[135-140]:

$$(CH_3)_3CX \rightarrow (CH_3)_3C^{\oplus}X^{\ominus} \rightarrow (CH_3)_2 = CH_2 + HX \quad .$$

The hydrogen halide formed reacts rapidly and quantitatively with (II).

The presence of protonated silanol groups on the surface of dispersed silica induces the reverse transition from the radical to the verdazyl cation[141].

The interaction of triarylverdazyls with thio-acids (dehydrogenation of the S–H bond) has been studied in relation to thiophenols. In polar solvents the reaction proceeds via the mechanism[142]:

$$V^{\cdot} + H{-}S{-}Ph \rightarrow VH + \dot{S}Ph \quad ,$$

$$\dot{S}Ph + \dot{S}Ph \rightarrow Ph{-}S{-}S{-}Ph \quad .$$

In non-polar solvents the reaction is reversible:

$$2V^{\cdot} + H{-}S{-}Ph \overset{K_p}{\rightleftarrows} VH + V{-}S{-}Ph \quad .$$

In the reaction with thiophenols triarylverdazyls behave as dehydrogenating agents in polar solvents and also as acceptors of the $PhS^{\cdot}$ free radicals in non-polar solvents[90,142]. The rate of dehydrogenation of thiophenols $v = k_2[V^{\cdot}][PhSH]$ depends on the nature of the substituent in the *p*-position of thiophenol and increases on passing from unsubstituted to substituted thiophenols, which is apparently due to the increase of stability after the introduction of substituents into the intermediate thiol radicals. In the reaction with thiophenols verdazyls behave as electron donors, and the effect of the substituent in the radical is satisfactorily described by the Hammett equation (Table 4)[218].

4. Dehydrogenation by Verdazyl Radicals and Cations

Verdazyls are readily reduced either in an acid medium[26,130] or when compounds with mobile hydrogen, for example hydrazine and phenylhydrazine, are used[2,80,90,143]. A characteristic feature of the reduction of triarylverdazyls as well as iminoxyls[25] is that their occurrence requires the presence of not only an electron donor, but also a proton donor[80,90]. Leucoverdazyls are readily oxidised by atmospheric oxygen to radicals and in the presence of alkalis the rate of oxidation increases sharply; thus verdazyls may be regarded as dehydrogenation catalysts:

$$V^{\cdot} + BH \rightarrow VH + B^{\cdot};\ VH \xrightarrow[O_2]{KOH} V^{\cdot} \quad .$$

Hydrazobenzene (HB) is a powerful reductant in relation to (II). The reaction kinetics have been studied in detail[144]. The rate of reaction is described by the equation $v = k_2[V^{\cdot}][HB]$ and depends little on the nature of the solvent§; as the electron-donating properties of the radical become more pronounced, the rate increases and there is a correlation of the rate constants both with σ constants and with the electrophilic σ^+ constants[147] (Table 4). There is also a correlation between $\lg k_2$ and the polarographic oxidation potentials of verdazyls (Table 4). The excellent correlation between the HB dehydrogenation rate constants and the electrophilic constants of substituents and the negative reaction constants ρ and α in Dimroth's equation shows that the structure $X^{\delta-}-H\ldots{}^{\delta+}V^{\cdot}$ makes a significant contribution to the transition state. It has been shown[90,129] that radicals (II) readily dehydrogenate compounds with acid or weakly basic properties.

The radical mobility of the hydrogen atom in the C–H bond has been studied in relation to the reaction of (II) with 1,4-dihydropyridines (DP), which are weak bases[148]. DP are analogues of biologically active compounds—coenzymes and dihydrocoenzymes. They exhibit striking electron- and hydrogen-donating properties and behave as hydrogen transferring agents in biological oxidation-reduction processes[148]. The kinetics of the reaction of (II) with *N*-benzyl-1,4-dihydronicotinamide (BDN) and 3,5-diethoxycarbonyl-2,6-dimethyl-1,4-dihydropyridine (Hantzsch ester, HE) have been studied in detail[90,129,149-156]. The rate of reaction is described by the equation $v = k_2[V^{\cdot}][DP]$ and depends significantly on the nature of the substituent in the 4-position of DP. For triarylverdazyls substituted in the *p*-position of the $C_{(6)}$-phenyl ring, a complete inversion of the activity series is observed on passing from DMF to C_2H_5OH [the values of k_2(rel.) are listed below]:

	bis-CH_3O*	CH_3O	H	Cl	NO_2
		DMF, 25°			
BDN	1	1.6	1.8	2.2	2.8
HE	1	1.9	2.0	2.2	2.7
		Alcohol, 25°			
BDN	2.9	1.7	1.4	1.1	1
HE	5.1	4.3	1.8	1.6	1

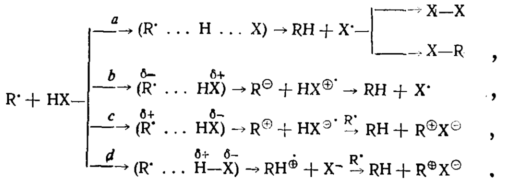
* 2,6-bis-(4-methoxyphenyl)-4-phenylverdazyl.

Such unusual behaviour of verdazyl radicals is associated with the enhancement of their nucleophilic properties on passing from DMF to alcohol[90]. The rate constants for the reactions in DMF and alcohol are correlated respectively with the σ and σ^+ constants of the substituents and the polarographic reduction and oxidation potentials of radicals (II) (Table 4). In DMF the verdazyls (II) behave as electron acceptors, while in alcohol they behave as electron donors. Variation of ρ and the zero value of the latter have been observed recently for reactions involving the abstraction of hydrogen from substituted toluenes on passing from methyl to t-butyl and heptyl radicals, which the authors also explained by the enhancement of the nucleophilic properties of the radicals[157].

The observed small effects of the substituents in the verdazyls can be explained by the closeness of the experimental temperature to the isokinetic temperature β [158] [when β is traversed, the activity of (II) is reversed[90] (Table 4)]. It must be emphasised that the isokinetic or isoequilibrium relations are some of the most important characteristics of reactions, being particularly necessary for the interpretation of the polar effects of substituents, whose influence on the rate of reaction depends significantly on the experimental temperature and on β.

Data for the dehydrogenation of the C–H bonds of DP by verdazyls show that the rate of abstraction of hydrogen is in this case lower than in the reaction with O–H and S–H acids and also with HB (N–H bonds). It appears that the polarity of the dissociated bond is important for hydrogen transfer reactions involving (II). Presumably in the first stages of the dehydrogenation reaction, radical (II) is solvated (a hydrogen bond is formed) by the molecule with which it subsequently reacts. In this case the formation of the hydrogen bond precedes the formation of the activated complex and such association facilitates the reaction to a large extent[5,159]. When hydrogen is abstracted from polar X–H bonds, the increasing contribution of the Coulombic interaction between $V^{\cdot}$ and X–H leads to a decrease of the barrier¶. In the transition state of the dehydrogenation reaction there is a possibility of a shift of electron density and of proton migration via the hydrogen bond, depending on the donor–acceptor properties of the reactions[160]. The rate of dehydrogenation of (II) is influenced mainly by the specific solvation of radicals, which thus exerts the principal influence on the initial state. The solvation of the activated complex is apparently slight[90]. For verdazyls, which are some of the most stable free radicals, the main role should be played by the polar effects of the reactants and the polarisability of the hydrogen donor molecule, in conformity with Hammond's postulate.

Examination of data for reactions involving the abstraction of hydrogen by stable radicals makes it possible to represent these reactions by the following schemes[5,90,129,159]:



$$R^{\cdot} + HX \xrightarrow{a} (R^{\cdot}\ldots H\ldots X) \rightarrow RH + X^{\cdot} \rightarrow X{-}X \text{ or } X{-}R \ ,$$
$$R^{\cdot} + HX \xrightarrow{b} (\overset{\delta-}{R^{\cdot}}\ldots \overset{\delta+}{HX}) \rightarrow R^{\ominus} + HX^{\oplus\cdot} \rightarrow RH + X^{\cdot} \ ,$$
$$R^{\cdot} + HX \xrightarrow{c} (\overset{\delta+}{R^{\cdot}}\ldots \overset{\delta-}{HX}) \rightarrow R^{\oplus} + HX^{\ominus\cdot} \xrightarrow{R^{\cdot}} RH + R^{\oplus}X^{\ominus} \ ,$$
$$R^{\cdot} + HX \xrightarrow{d} (R^{\cdot}\ldots \overset{\delta+}{H}{-}\overset{\delta-}{X}) \rightarrow \dot{R}H^{\oplus} + X^{-} \xrightarrow{R^{\cdot}} RH + R^{\oplus}X^{\ominus} \ .$$

They describe the possible pathways in free-radical substitution. Pathway *a* presupposes radical abstraction of hydrogen via the intermediate formation of a symmetrical activated complex. The interaction of $R^{\cdot}$ with hydrogen donors can proceed with appreciable charge separation in the transition state (*b*, *c*, and *d*). The radical behaves as an electron acceptor (*b*), an electron donor (*c*), and a proton acceptor (*d*) (*c* and *d* differ little). The choice of reaction pathway depends on the donor–acceptor properties of the reactants, the polarity of the medium, and other reaction conditions. The structure $X^{\delta-}-H^{\delta+}\ldots R^{\cdot} \rightleftharpoons X^{\delta-}\ldots HR^{\cdot\delta+}$ may contribute significantly to the transition states of the (II) dehydrogenation reactions. However, it is not clear how to reconcile the low reaction constants (Table 4) and the correlation with the σ^+ constants, indicating the localisation of a large positive charge at the reaction centre[161].

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§ This was also observed in the dehydrogenation of the tetrazines (II).[145,146]

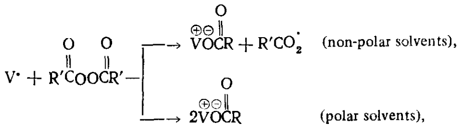
¶ In this case E_a increases in the following sequence of bonds: O–H < N–H < S–H < C–H.

In the excited state (I) readily dehydrogenates various hydrocarbons with which it does not react under the usual conditions[29].

The possibility of acid catalysis of radical reactions was demonstrated for the reactions of nitrogen oxides with amines and diamines[5]. Acid catalysis of reactions involving verdazyls takes place particularly readily because of the high rate of reaction of (II) with acids. The radical reaction pathway then changes to an ionic pathway, and the rate of reaction increases markedly[129,162]. The rate of dehydrogenation of DP on passing from (II) to verdazyl salts increases by a factor of 10^6–10^7.[90,129,155,163] The substituent in the 4-position of HE has a significant influence on the rate of reaction, which changes by a factor of 10^5 when R=H is replaced by R = C_6H_5.[164] In the reaction with a verdazyl salt the effect of the substituent in the *p*-position of the phenyl ring in the 4-position in HE is described by the Hammett and Dimroth equations (Table 4). The ease of the hydride shift reaction is due to the conversion of DP into a stable pyridinium salt[148]. The data obtained for the influence of the substituent in the 4-position in DP on the rate of reaction with (II) and verdazyl salts are in good agreement with quantum-chemical calculations, showing that the most reactive atom in the pyridine ring is the carbon atom in the 4-position[148]. Different catalytic processes occurring with participation of coenzyme models are also determined by the presence of this carbon atom. It appears that the rest of the molecule—the adenine ring and the phosphate chain—merely facilitates fixation on the protein. The use of verdazyls in the study of electron and hydride transfer with participation of DP may be of interest for the elucidation of the causes of the catalytic action of enzymes incorporating various coenzymes[148].

5. Reactions of Verdazyls with Peroxy-Compounds

The reaction of verdazyl radicals with peroxy-compounds is regarded as bimolecular homolytic substitution $S_{H}2$ at the oxygen atom[125]. It has been shown[109,112,113,125,165–169] that verdazyls readily induce the decomposition of diacyl peroxides:



$$V^{\cdot} + R'\overset{O}{\overset{\|}{C}}O O\overset{O}{\overset{\|}{C}}R' \begin{cases} \longrightarrow \overset{\oplus\ominus}{V}O\overset{O}{\overset{\|}{C}}R + R'CO_2^{\cdot} & \text{(non-polar solvents),} \\ \longrightarrow 2\overset{\oplus\ominus}{V}O\overset{O}{\overset{\|}{C}}R & \text{(polar solvents),} \end{cases}$$

where R′ = Ph, C_6H_{13}, or $C_{11}H_{23}$. The benzoyloxy-radical $PhCO_2^{\cdot}$, formed in non-polar solvents, has been identified on the basis of its decomposition products[125]. The verdazyl salts $V^{\oplus}{}^{\ominus}O_2CR'$ are relatively unstable and undergo further reactions associated with the opening of the verdazyl ring and the formation of formazans[125]. The rate of reaction of (II) with diacyl peroxides is described by the second-order equation $v = k_2[V^{\cdot}][\text{peroxide}]$, the stoichiometry of the reaction being represented by $[(II)]/[\text{peroxide}] = 1:1$ in non-polar solvents [this made it possible to recommend (I) as an analytical reagent for the determination of low concentrations of benzoyl peroxide (BP)][170] and ~2 : 1 in polar solvents[165,166], which is due to the stability of the radical $R'CO_2^{\cdot}$. Thermal decomposition of diacyl peroxides takes place at an appreciable rate only at elevated temperatures (70–80°C). Thus $k_1 = 4.8\times10^{-8}\ s^{-1}$ and $E_a = 30$ kcal $mole^{-1}$ for BP in benzene at 30°C;[171] the decomposition of BP induced by (II) is approximately 10^9 faster, which is due to the sharp decrease of E_a to 5–8 kcal $mole^{-1}$.

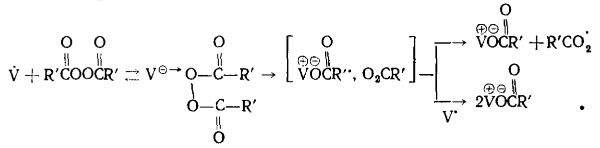
The rate of oxidation of verdazyls by BP depends little on the nature of the solvent, and the changes in the rate are not associated with the influence of the polarity of the medium, but are due to the specific solvation of (II). The relatively low activation entropy $\Delta S^{\neq} = -(29–33)$ e.u. indicates the formation of a fairly ordered transition state. In an alcoholic medium the reaction with BP leads to the regeneration of (I),[172] which is associated with the interaction of the reaction products (verdazyl salts) with alcohol molecules, the process being strongly accelerated by alkali (KOH).[125]

The rate of reaction of (II) with diacyl peroxides depends little on the nature of the substituent in the $C_{(6)}$-phenyl ring of (II) and increases as the electron-donating properties of the substituents become enhanced. The validity of the Hammett and Dimroth correlation equations and the isokinetic relation (Table 4) indicates a unique oxidation mechanism for all verdazyl radicals.

As the electron-accepting properties of substituents in BP become more marked (i.e. as the peroxy-oxygen becomes more electrophilic), the rate of reaction rises and the effect of the substituent is described by the Taft equation (which is probably associated with attack on the peroxy- and not the carbonyl oxygen atom) (Table 4). The rates of reaction of substituted BP with radicals (II) are satisfactorily correlated with the potentials $E_{1/2}$ for the reduction of peroxides[173]. The high values of α in the Dimroth equation, amounting to approximately 30, are striking (Table 4).

Special experiments established that the molecular rearrangement of the peroxide (carboxy-inversion) takes place very slowly and does not affect the rate of the reaction with verdazyls considered here[174].

On the basis of the results, the following mechanism has been proposed for the interaction of verdazyl radicals with diacyl peroxides[125]:



$$\dot{V} + R'\overset{O}{\overset{\|}{C}}O O\overset{O}{\overset{\|}{C}}R' \rightleftarrows V^{\ominus}\!\rightarrow O\!-\!\overset{O}{\overset{\|}{C}}\!-\!R' \atop \quad\;\; O\!-\!\underset{\underset{O}{\|}}{C}\!-\!R' \rightarrow \left[\overset{\oplus\ominus}{V}O\overset{O}{\overset{\|}{C}}R'^{\cdot},\ O_2CR'\right] \begin{cases} \longrightarrow \overset{\oplus\ominus}{V}O\overset{O}{\overset{\|}{C}}R' + R'CO_2^{\cdot} \\ \xrightarrow[V^{\cdot}]{} 2\overset{\oplus\ominus}{V}O\overset{O}{\overset{\|}{C}}R' \end{cases}.$$

In the rate-determining stage of the reaction (II) attacks the peroxy-oxygen. Experiments using BP labelled with ^{18}O in the carbonyl group have shown that attack by trialkylstannyl and triphenylmethyl radicals also takes place at the peroxy-oxygen[120]. Quantum-chemical calculations, indicating a deficiency of electron density in the peroxy-linkage, are consistent with this finding[175]. The weak influence of the polarity of the medium and the low reaction constants ρ in the Hammett and Taft equations may indicate the formation of a weakly polar transition state in this reaction, i.e. the rate-limiting stage is the formation of a complex and electron transfer takes place in subsequent rapid stages. In weakly polar solvents the radical-ion pair formed is unstable and undergoes further transformations, while in polar and $R'CO_2^{\cdot}$ stabilising solvents, $R'CO_2^{\cdot}$ reacts with a second verdazyl radical.

It is noteworthy that the mechanism involving electron transfer in the rate-limiting stage (*SET*) has been quite adequately demonstrated for reactions involving the oxidation of amines by organic peroxides[171,176]. According to the authors, the validity of this mechanism is proved by correlations of the Hammett, Taft, and Dimroth types, as well as correlations between the rate constants and the ionisation potentials and electron affinities. Furthermore, the reactions of free radicals and peroxides may involve either homolytic substitution or electron transfer, but one cannot draw a sharp boundary between them. When a complex is formed, a structure with charge separation, the extent of which is determined by the donor–acceptor properties of the reactants and other reaction conditions, may make a considerable contribution to the transition state. In many cases, the reaction is preceded by the formation of a loose complex between the reactants, and electron transfer is the rate-limiting stage[177]. A weak influence of the dielectric constant ϵ of the medium may be observed when the energy of the transition state is closer to the initial state on the reaction coordinate than to the final state. The structure of the transition state then resembles that of the initial compounds and the polar effects of the medium play a small role according to Hammond's postulate.

It is noteworthy that neither the reaction products, nor the effect of solvent polarity[177], nor the existence of various correlation equations, nor the coefficients in these equations[167] can serve as exclusive evidence for reactions involving a one-electron transfer mechanism and do not allow a choice of a particular mechanism.

6. Complex Formation

The solvent is known[5,178] to be capable of influencing significantly the kinetics and mechanism of radical liquid-phase reactions, which is attributed mainly to its ability to form hydrogen-bonded and π- or n-complexes. The formation of complexes of stable radicals with solvent molecules† as a rule leads to an appreciable decrease of their reactivity. The experimentally observed effective rate constant is expressed by a complex combination of the rate constants for the reactions of non-solvated and solvated molecules, the equilibrium constants for the complex formation reactions, and the coordination numbers of the solvate[5,178]. The formation of π-complexes is well known for many stable radicals[5]. The rates of dehydrogenation of HB [144] and dihydropyridines[90,156] and of the reactions with BP [165] and with lauroyl peroxide[109], involving triarylverdazyls, decrease appreciably on passing from hydrocarbons to π- and n-donor solvents.

The formation of π- and n-complexes of triphenylverdazyl and the kinetic manifestations of such complex formation have been investigated by spectroscopic and kinetic methods for reactions carried out in mixed solvents[109,156,169,179]. As for other stable radicals[5,178], association with only one molecule of the complex-forming solvent is significant for (I). The rate constants for the solvated radicals (I) are smaller by 1–2 orders of magnitude than those for the non-solvated radicals[109,156,169]. With increase of the concentration of the π- and n-donor solvents in the mixture, there is a parallel increase of E_a [90,109] (which may be attributed to the necessity for the dissociation of the radical–solvent complexes) and of $\Delta S^{\neq}$ (desolvation preceding the formation of the transition state leads to disordering of the system[5,178]). The formation of π-complexes of (I) in aromatic solvents is accompanied by a bathochromic shift of the $\pi \rightarrow \pi^*$ absorption band, and a decrease of the molar extinction coefficients at λ_{max} compared with spectra recorded in hexane[156,169]. The thermodynamic constants for the formation of the complexes as well as the difference between the bond energies of the complex in the ground and excited states[108], i.e. $\Delta H_g - \Delta H_e = h(\nu_0 - \nu_S)$, where ν_0 and ν_S are the frequencies at the electronic band maxima of (I) in hexane and in a solvating solvent, as well as the equilibrium constants for the solvation of (I) in the ground and excited states, i.e.

$$V^{\cdot} + S \overset{K_g}{\rightleftarrows} V_s^{\cdot} \quad ,$$

$$V^{\cdot *} + S \overset{K_e}{\rightleftarrows} V_s^{\cdot *} \quad ,$$

where K_g and K_e are the equilibrium constants for the solvation of (I) in the ground and excited states and S is the solvent, may be determined from the absorption spectra of (I) in mixed solvents. The formation of π-complexes by (I) with benzene and pyridine causes a bathochromic shift; $\Delta H_e - \Delta H_g$ is 2.4 kcal mole^{-1} in benzene and 4.0 kcal mole^{-1} in pyridine[156,169], i.e. the stabilities of the π-complex of the excited (I) in benzene and pyridine exceed by 2.4 and 4.0 kcal mole^{-1} respectively the stability of the π-complex in the ground state. There is an increase in the equilibrium constants for solvation in the excited state [$\ln K_e/K_g = (\Delta H_e - \Delta H_g)/RT$][180] and the dipole moment (~9 D) [29] on photoexcitation of (I).[29]

Table 5. Thermodynamic parameters of the complexes of stable radicals with organic solvents[219].

Solvent	$K_{25°}$ *, litre mole^{-1}	$-\Delta H°$, kcal mole^{-1}	$-\Delta S°$, e.u.	$\Delta G°$, kcal mole^{-1}
	t-Butyl mesityl nitroxide (Ref.181)			
Benzene	0.14	5.8	23.6	1.2
Chlorobenzene	0.18	3.5	15.2	1.0
Bromobenzene	0.22	2.2	10.5	0.9
Styrene	0.15	1.5	8.7	1.1
Methyl methacrylate	0.18	4.4	18.1	1.0
Methyl acrylate	0.45	10.9	38.1	0.5
Methylacrylonitrile	0.15	7.1	27.6	1.1
	Triphenylverdazyl (Refs. 155 and 169)			
Benzene	0.26	1.5	7.7	0.8
Anisole	0.45	0.9	4.7	0.5
Pyridine	0.41	2.6	10.7	0.6
	Phenoxyls (Ref.182)			
Nitrobenzene**	0.37	1.6	7.3	0.6
Nitrobenzene ***	0.81	1.4	5.0	0.1
Nitrobenzene****	1.0	2.5	8.3	0
	Dianisyl nitroxide (Ref.183)			
Benzene	0.15	6.2	24.6	1.1

* At the isoequilibrium temperature $\beta = 283$ K, we have $\ln K_p = 1.0 \pm 0.4$, which does not allow sufficiently rigorous inferences concerning the isoequilibrium conditions[158].

** 2,4,6-Tri-t-butylphenoxyl.

*** 2,6-Di-t-butyl-4-phenylphenoxyl.

**** Galvinoxyl

Since the initial state in radical reactions frequently involves a higher degree of solvation than the transition state, an increase of solvation causes an increase of E_a and makes the process less exothermic[109,156,169]. Solvation also leads to a weakening of the electrophilic or nucleophilic properties of the radicals and to a diminution of the role of polar influences[90,107,178].

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† The dissolution of any substance B is accompanied, in principle, by solvation and the formation of a solvate complex having the average composition $B_{solid} + nS \rightleftharpoons BS_n$.

Table 5 presents the thermodynamic parameters for the formation of complexes by (I) and other stable radicals in π-donor solvents (the solvation equilibrium constants were determined from chromatographic[181], kinetic[182], and spectroscopic data[183]). The enthalpies and entropies of the complex formation reactions vary in parallel—the higher the heat of formation of the complex the lower the value of $\Delta S°$. The most stable complex is that of t-butyl mesityl nitroxide with methyl acrylate. The relation between $\Delta H°$ and $\Delta S°$ for the π-complex formation reactions of stable radicals (14 complexes) is satisfactorily described by the equation[219]

$$\Delta H^0 = 0.283\Delta S^0 - 0.535 \; (r = 0.992, \; s_0 = 0.377).$$

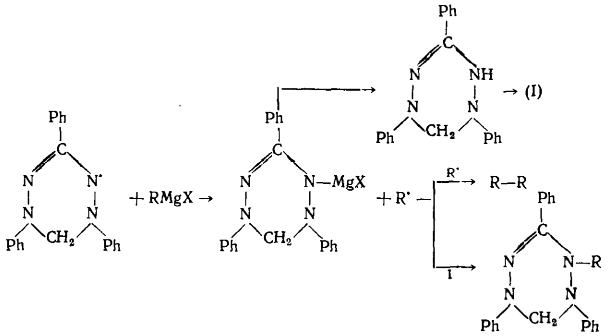
The isoequilibrium temperature β = 283 K. The free energies of formation of the complexes change comparatively little ($\Delta G°$ = 0.8 ± 0.4 kcal mole^{-1}), which is due to the closeness of the experimental temperature to β. Presumably the linear relation between $\Delta H°$ and $\Delta S°$ is a characteristic feature of the thermodynamics of the formation not only of complexes of the donor–acceptor type[184] but also of other complexes having similar structures and compositions.

The elucidation of the nature of the complexes formed by radicals with the molecules of organic solvents is important for the theory of reactivity. It has been observed for certain radicals, particularly DPPH and phenoxyls[178], that the hyperfine interaction in the EPR spectra depends on the nature of the solvent. This indicates partial electron transfer on complex formation. Virtually no changes in the hyperfine interaction constants in electron-donating solvents have been observed for (I).[90,109,156] Specific intermolecular interactions (van der Waals and dipole–dipole interactions as well as interactions involving polarisation forces) may play a significant role in the formation of complexes by radicals with solvent molecules[185]. When a π-complex of the radical and solvent molecules is formed, the π orbitals of the radical and the ligand overlap, which leads to paramagnetic shifts of the NMR lines and a change in the T_1 and T_2 relaxation times of the ligand nuclei, and is responsible for dynamic nuclear polarisation (DNP).[5] DNP studies on many radicals in electron-donating solvents have shown that the degree of transfer of the unpaired electron in the π-complex is small[5,178]. A DNP study on verdazyls led to the discovery of a large contribution of the contact interaction to nuclear polarisation, which is associated with the high spin density in the verdazyl ring[63,64]. The presence of a spin density in the ligand causes either spin polarisation of the C–H bonds or the density spreads via a hyperconjugation mechanism.

The steric orientations of the radical and the ligand are very important in the delocalisation of the unpaired electron. The orientations of the complexes of radicals with solvent molecules obey a statistical distribution[186]. The most stable configuration in this distribution is not optimal either from the standpoint of charge transfer or the pre-reaction complex. There is no reaction within the π-complex, as shown by Russell in chlorination reactions and by Buchachenko and Sukhanova[187] in the reaction involving the abstraction of hydrogen from ethylbenzene by an *N*-oxide radical.

7. Reactions of Verdazyls with Organometallic Compounds

Kinoshita and coworkers[40,43] showed that polymers incorporating the tetrazine structure are formed in the initiation of the anionic polymerisation of vinyl monomers incorporating the verdazyl structure by Grignard reagents, alkyl-lithium compounds, and sodionaphthalene. It is suggested that the reactions of triarylverdazyls with organolithium compounds (EtLi, BuLi), organoaluminium compounds [$Al(C_2H_5)_3$, $Al(C_2H_5)_2Cl$, $Al(t\text{-}C_4H_9)_3$, or Grignard reagents (ethyl-, isopropyl-, or butyl-magnesium bromides, benzylmagnesium chloride) proceed via the intermediate formation of a metallic salt of the verdazyl and be treated as free-radical substitution at the nitrogen atom[188-191]. The following mechanism of the reaction with (I) has been proposed for organomagnesium compounds, for example on the basis of the analysis of the reaction products:

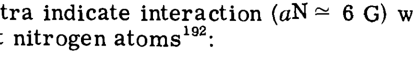


R=C_2H_5, iso-C_3H_7, n-C_4H_9, iso-C_4H_9, t-C_4H_9, CH_2Ph, or CH_2CH_2Ph.

Metal salts of the verdazyl (I) are unstable and readily hydrolyse with formation of leuco-bases, which are oxidised to (I).

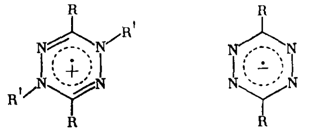
V. TETRAZINYL RADICAL-IONS AND TETRA-AZAPENTENYL, TETRAZOLINYL, AND PHOTOTETRAZOLINYL RADICALS

Cyclic compounds with four nitrogen atoms (tetrazines and tetrazolium salts) as well as their linear analogues (formazans and tetra-azapentenyls) show a very high tendency towards the formation of radical structures, because of the possibility of a marked delocalisation of the unpaired electron, which lowers the energy of the ground state of the system. Thus stable (withstanding boiling) radicals are formed readily in dioxan solutions of copper dithizonate and diphenylcarbazonate complexes. The EPR spectra indicate interaction (aN ≃ 6 G) with the four equivalent nitrogen atoms[192]:



$$R{-}S{-}C{\begin{smallmatrix} \nearrow N{-}\dot{N}{-}Ph \\ \searrow N{=}N{-}Ph \end{smallmatrix}} \qquad H{-}O{-}C{\begin{smallmatrix} \nearrow N{-}\dot{N}{-}Ph \\ \searrow N{=}N{-}Ph \end{smallmatrix}} \quad R{=}H,\ CH_3 \cdot$$

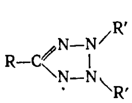
The *sym*-tetrazine/1,4-dihydro-*sym*-tetrazine system is of the oxidation-reduction type (like the quinone/hydroquinone system) and readily forms radicals[193-195]. The one-electron oxidation of 1,4-dihydro-*sym*-tetrazines leads to relatively stable radical-cations. The hyperfine interaction constants are $a^N_{1,5}$ = 7.4–8.0 G and $a^N_{2,4}$ = 3.4–4.5 G depending on the substituents. When *sym*-tetrazines are reduced by alkali metals, fairly stable radical-anions are formed:



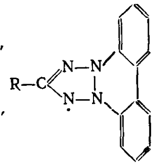
R = CH$_3$, or Ph, R' = H; R, R' = Ph;

R = Me, Et, iso-Pr, or (Ph)$_2$CH .

The first stable tetrazolinyl and phototetrazolinyl radicals [(XVIII) and XIX) respectively] were synthesised by Kuhn and coworkers[196]:

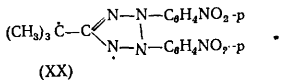


(XVIII)



(XIX)

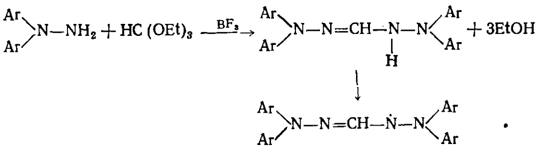
The triphenyltetrazolinyl radical is stable in air and its EPR spectrum indicates the interaction of the unpaired electron with the two pairs of equivalent nitrogen atoms ($a^N_{2.3}$ = 7.5 G, $a^N_{1.4}$ = 5.6 G). The radicals are readily obtained on reduction of tetrazolium and phototetrazolium salts or on homolytic abstraction of hydrogen from formazans, or on their oxidation to tetrazolium salts[197–199]. Intramolecular electrochemical cyclisation of formazans to tetrazolium salts proceeds via the intermediate formation of radical-cations[200]. It has been shown that the tetrazolium radicals formed on oxidation of formazans, on reduction of tetrazolium salts, on disproportionation of a mixture of a formazan and a salt, and on homolytic abstraction of hydrogen from formazan have cyclic structures[201]. Only one stable tetrazolinyl radical, namely radical (XX), has been isolated in a crystalline state[202]:



(XX)

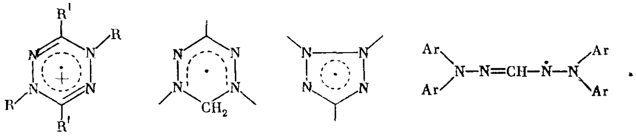
A study of the magnetic susceptibility of (XX) showed that[198] it is monomeric in solution. The stability of tetrazolinyl radicals increases as the electron-accepting properties of the substituents in the N-phenyl rings become more pronounced and $a^N_{2.3} > a^N_{1.4}$ for both tetrazolinyl and phototetrazolinyl radicals.

Apart from cyclic radicals with four nitrogen atoms, their linear analogues (tetra-azapentenyl radicals) are also known[203–205]. They are obtained by oxidising with oxygen, silver oxide, or lead dioxide the products of the condensation of orthoformic ester with an asymmetric hydrazine:



These radicals have a bluish-green colour (λ_{max} = 600–700 nm) and are much less stable than their cyclic analogues. Some of them, for example 1,1,5,5-tetraphenyl-1,2,4,5-tetra-azapentenyl, are stable and can exist for weeks in a crystalline form. In solution tetra-azapentenyls are monomeric and obey the Beer–Lambert law.

Comparison of the EPR spectra of verdazyls, tetrazinyl radical-ions, tetrazolinyl radicals, and tetra-azapentenyls illustrates the significant influence of the delocalisation of the unpaired electron on the stability of the radicals. All the radicals and radical-ions have seven π electrons and an insignificant spin density at the ring carbon atoms:



Most of the spin density is located at the terminal nitrogen atoms of the hydrazidinyl system[6]: $a^N_{1.5}/a^N_{2.4}$ is ~1 for verdazyls, ~1.7 for tetra-azapentenyls, and ~2 for tetrazinyl radical-cations; $a^N_{2.3}/a^N_{1.4}$ is ~1.3 for tetrazolinyls and ~2 for phototetrazolinyls. Electron-accepting substituents in the benzene ring cause a partial withdrawal of electron density from the central ring and tend to make the nitrogen atoms equivalent; the stability of tetrazolinyls and phototetrazolinyls then increases.

VI. PRACTICAL ASPECTS OF THE CHEMISTRY OF VERDAZYL RADICALS

The vigorous development of the chemistry of verdazyls is associated with the important role which they play in the solution of various theoretical and practical problems.

Verdazyls proved to be convenient objects for the solution of many problems in theoretical chemistry (the determination of the mechanisms of elementary chemical reactions, the determination of the relation between the reactivity and structure of reagents, and the study of the propagation of π- and σ-electron spin density, intermolecular interactions, weak exchange interactions of electrons, ferromagnetic interactions, etc.). In many cases it has been possible to elucidate in relation to verdazyls the influence of solvent polarity, π- and n-complex formation, and hydrogen bonds on the kinetics of liquid-phase radical reactions. The important role of polar factors (and of the isokinetic temperature in their interpretation) in the kinetics and mechanisms of homolytic reactions has been demonstrated. Verdazyls are convenient spin labels for the study of the dynamic structures of polymers in solutions; verdazyl bi- and tri-radicals are used to study the structures and molecular motions in isotropic and liquid-crystal solutions[206,207], which is of interest for structural chemistry, because it makes it possible to determine the number of unpaired electrons and the average distance between them.

As a result of the discovery of methods for the synthesis of verdazyls without affecting the free valence, it is possible to obtain spin-labelled compounds, so that verdazyls are likely to be useful in molecular biology, biophysics, the physical chemistry of polymers, the synthesis of spin-labelled drugs, and models of physiologically active compounds, and in the study of the mechanism of the action by EPR.

Verdazyls can be used in analytical chemistry as indicators[217]. In view of their very high stability, ready availability, and the possibility of obtaining them as 100% pure preparations, verdazyls are likely to be useful as standards in quantitative measurements by EPR (the percentage content of DPPH, for example, varies markedly with time[208]). The possibility of using verdazyls in laser engineering has been investigated[209]. Being stable over a wide range of potentials (~1 V), triphenylverdazyl may be used as a "trap" for short-lived radicals obtained in electrode reactions (DPPH, for example, is electrochemically stable only in the region of ~0.3 V).[97]

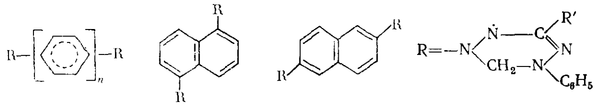
Pokhodenko et al.[210] showed recently that, in the electron transfer reaction between two stable radicals one of which is triphenylverdazyl, an e.m.f. ranging from several tenths of a volt to several volts is generated. The formation of reversible galvanic cells based on stable radicals or radical-ions[211] is of considerable theoretical and practical interest.

The use of verdazyls as dyes is promising. In contrast to DPPH, verdazyls dye fabrics uniformly, which permitted their employment for the study of the wear of knitted materials[212]. The ability of verdazyls to dye polymeric materials may prove useful in the study of the mechanical degradation of polymers by EPR.

Verdazyls react with many compounds which are sources of free radicals: peroxides, hydroperoxides, and transition metal compounds. The properties of verdazyls as free radical acceptors permit the study of cell effects in the decomposition of initiators of radical polymerisation and the dependence of the yield of radicals on the nature of the solvent. The ability of verdazyls to terminate kinetic chains by reacting with active radicals makes it possible to use them as inhibitors of autoxidation and radical polymerisation. Thus the polymerisation of styrene in the presence of triphenylverdazyl (1 : 30 000) is strongly inhibited and the autoxidation of benzaldehyde at 20°C is fully suppressed[2]. Water-soluble verdazyls inhibit the decomposition of H_2O_2 initiated by catalase or platinum black[26]. Verdazyls inhibit effectively the polymerisation not only of styrene but also of other monomers—methyl methacrylate, acrylonitrile, vinyl chloride, and vinyl acetate. In the presence of (I) polarisation is fully suppressed and after its consumption takes place at the same rate as in the absence of added inhibitor. The induction period increases linearly with increasing concentration of (I) for the same initiator concentration, which shows that, in contrast to aliphatic nitroxides, (I) does not undergo side reactions. The linear dependence of the induction period on the verdazyl concentration shows that these radicals initiate the formation of kinetic chains to only a slight extent[115]. The period corresponding to inhibition by verdazyls may be measured spectroscopically and verdazyls can thus be used to determine the rate of initiation. In contrast to hydroxylamines, leucoverdazyls do not affect the induction period but inhibit polymerisation effectively. The activities of various inhibitors of radical polymerisation have been compared in relation to the polymerisation of oligourethane-acrylate initiated by azobisisobutyronitrile. Verdazyl mono- and bi-radicals are powerful inhibitors[213,214]. Its high effectiveness, the simplicity of its synthesis, its ready availability, and the possibility of the visual monitoring of its concentration made it possible to recommend triphenylverdazyl as a promising stabiliser in the manufacture, storage, and processing of many oligomeric and monomeric compounds[214].

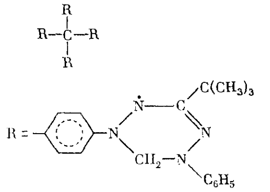
The development of research into polymers with stable radicals in the main or side chains was stimulated by the great interest in new semiconducting materials. Polymers with verdazyl radicals (molecular weight 2300–4800) as well as oligomers containing verdazyls in the polymer matrix are of interest from the standpoint of their electrical properties, radical reactions, and practical employment as antioxidants, redox indicators, and catalysts of certain oxidation-reduction reactions[36-45,115-117,215].

During the preparation of the manuscript for the press, a number of studies devoted to the chemistry of verdazyl radicals were published. New verdazyls containing heteroaromatic substituents in the 1-position of the formazan group[220,221] and triarylverdazyl radicals with perfluorophenyl substituents[222] were synthesised. New verdazyl biradicals have been obtained from the corresponding diformazans or monoverdazyls using a 1-cyano-1-methylethyl protecting group[223]:



R' = C_6H_5, or $C(CH_3)_3$.

Neugebauer et al.[224] recently obtained the tetraverdazyl (XXI), which is readily soluble in organic solvents:



4-Verdazyl[2,2]paracyclophanes have been obtained in order to study the characteristics of the distribution of spin density and interactions involving charge transfer[225]. The magnetic properties, ENDOR spectra, and characteristics of the intermolecular interactions of verdazyls with C_6H_6 and CCl_4 have been investigated[226-228].

Studies on the chemical properties of verdazyls have been developed further. It has been observed[229] that triphenylverdazyl catalyses the dark PI_3 polymerisation reaction in hexane, forms complexes with molecular oxygen[230], and decomposes peracids[231]. Triphenylverdazyl reacts reversibly with hydroquinone[232] and forms dicyanodiaziridine in the reaction with bromodicyanomethane[233]. The regeneration of verdazyls in reactions with peroxy-compounds, discovered by Yarmolyuk[125], has been investigated[234,235]. A study has been made of the influence of the composition of binary solvents on the kinetics of chemical reactions with participation of verdazyls[236-238]. The oxidation-reduction reactions of verdazyls have been investigated[239,240]. Quantum-chemical calculations on verdazyl radicals, ions, and leuco-compounds by the INDO method with total optimisation of the geometry, which made it possible to calculate their electronic and steric structures, can serve as a basis for the understanding and prediction of the chemical properties and reactivities of these species[241,242].

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Spectroscopic and Quantum-chemical Studies on the Active Centres in Anionic Polymerisation

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The mechanisms and consequences of complex formation in systems incorporating organometallic compounds are discussed on the basis of spectroscopic and quantum-chemical characteristics of alkyl, alkenyl, and aryl derivatives of lithium and certain other metals in the absence and presence of electron donors. Particular attention is devoted to "living" anionic chains. The bibliography includes 129 references.

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I. INTRODUCTION

Many of the anionic polymerisation processes initiated by organometallic compounds take place with participation of "living" polymers, i.e. growing chains which retain their capacity for the propagation reaction even after the complete exhaustion of the monomer or after the attainment of a state of equilibrium in the polymer–monomer system. In order to determine the relation between the experimental effects observed in such processes and the characteristics of the growing chains active in the system, it is necessary to investigate independent physicochemical characteristics of the corresponding "living" polymers. The first information of this kind was restricted to conductimetric data for and the electronic spectra of solutions containing agents of this kind. The constants for the dissociation into free ions were determined on the basis of such data for a number of compounds and the type of the initial ion pairs, which can be either contact or solvent-separated pairs of specially introduced electron donors (ED), was established[1]. In subsequent years these characteristics were supplemented by infrared and NMR spectroscopic data, which made it possible to improve significantly the available knowledge of the structure of the anionic active centres, particularly for metal alkenyls and their complexes with electron donors. The formulation of correct conclusions concerning the structure of the active centres requires information about the low-molecular-weight organometallic compounds which initiate anionic polymerisation. A survey of the available information about the infrared and NMR spectra of the above agents is the main subject of the present review. Due attention has been devoted to the results of theoretical calculations of the electronic structures and geometries of the agents simulating anionic active centres. Both experimental and calculated characteristics of compounds of the above type are known mainly for lithium derivatives.

II. LOW-MOLECULAR-WEIGHT ORGANOMETALLIC COMPOUNDS

1. Lithium Alkyls

The compounds RLi are known to be strongly associated in hydrocarbon solutions, the size of the aggregate being determined by the structure of R.[2-4] According to modern ideas, the association is due to the formation of many-centre linkages involving the vacant *p* orbitals of the lithium atoms and the sp^3 orbitals of the carbon atoms. Depending on the degree of branching of R and the nature of the medium, hexa-, tetra-, di- and mono-meric forms of RLi may exist[4]. In non-polar media the hexamers and the tetramers predominate for straight-chain and branched groups respectively. There is a mobile equilibrium between the different forms, which has been described in terms of dissociation via dimeric forms[5] and, according to Brown[3], the fastest exchange with a low activation energy occurs when the system contains hexamers:

$$(RLi)_6 \rightleftarrows (RLi)_4 + (RLi)_2, \tag{1}$$

$$(RLi)_2 + (RLi)_6 \rightleftarrows 2\,(RLi)_4. \tag{2}$$

The C–Li bond in lithium alkyls is a polar covalent linkage[1,4]. The carbon in the α-position relative to lithium is sp^3-hybridised in lithium alkyls and sp^2-hybridised in lithium aryls, which follows from a comparison of the α-^{13}C chemical shifts in the spectra of the lithium compounds with data for the corresponding hydrocarbon. The characteristics of certain compounds RLi obtained by NMR are presented in Table 1†.

Table 1. The differences between the chemical shifts ($\Delta = \delta_{RH} - \delta_{RLi}$, p.p.m.) in the ^{13}C NMR spectra of the compounds RLi and the corresponding hydrocarbons in benzene[6].

R	α–C	β–C	γ–C	δ–C	R	α–C	β–C	γ–C	δ–C
$(CH_3)_2CH$	−5.9	+8.1	—	—	$CH_3CHCH_2CH_3$	(−8)	+6.3; +6.0*	+2.6	—
$CH_3CH_2CH_2CH_2$	−1.4	+6 9	+6.4	+0.7	$(CH_3)_3C$	−10.7	+9.0	—	—

* For the CH_3 group.

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† The chemical shifts in all the Tables are quoted in terms of the δ scale.

It follows from the NMR data[6,7], that n-butyl-lithium (BuLi) differs from s- and t-BuLi and isopropyl-lithium (iso-PrLi) by the absence of spin–spin splitting due to the $^{13}C{-}^{7}Li$ bond, which can be in principle accounted for by a rapid intermolecular exchange[6] via the mechanism described by Eqns. (1) and (2). On the other hand, in solutions of iso-PrLi the hexameric form is also present[8], but the natures of the NMR spectra of the compounds iso-PrLi and BuLi are different. The infrared method makes it possible to determine the fraction of the associated species $(iso\text{-}PrLi)_n$ differing in the value of n, because the stretching vibrations of the Li–C bond in the tetramer and the hexamer are characterised by absorption bands at 475 and 510 cm^{-1} respectively[9] (Fig. 1)‡.

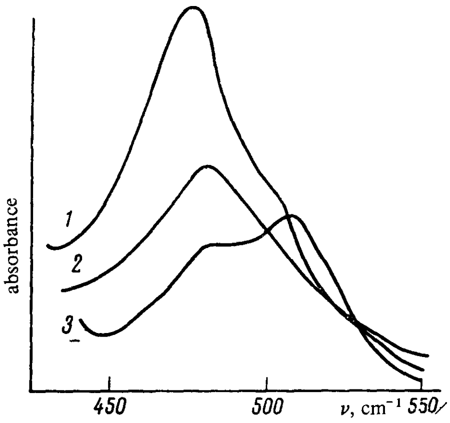

Figure 1. Infrared spectra of isopropyl-lithium in iso-octane[9]; concentration (M): 1) 0.24; 2) and 3) 1.2; temperature (°C): 1) −100; 2) 12; 3) 1.2.

The correct assignment of the ν(C–Li) absorption bands was carried out for the first time by West and Glaze[11] on the basis of the method involving the isotopic substitution of ^7Li and by ^6Li and of H by deuterium. The infrared characteristics of a number of compounds RLi are now known (Table 2). In his study of the reaction between the $CH_3^{\cdot}$ radical and metallic lithium in a solid argon matrix, Andrews[12] isolated the absorption bands due to CH_3Li in the infrared spectra. Comparison of his values with data for solid methyl-lithium[11] led him to the conclusion that the hypsochromic shift of the ν(C–Li) band in the spectrum of monomeric CH_3Li, greater than by 100 cm^{-1}, is due to the decrease of the C–Li bond length to 2.10 Å (compared with 2.28 Å in solid CH_3Li); this effect decreases the force constant. The nature of the C–Li bond vibrations in the associated species is complicated by the interaction of the vibrations of the fragments of the associated molecules.

Table 2. Stretching vibration frequencies of the C–Li bond (cm^{-1}) in the compounds RLi in a hydrocarbon medium.

R	$\nu(C{-}^7Li)$	$\nu(C{-}^6Li)$	Refs..	R	$\nu(C{-}^7Li)$	$\nu(C{-}^6Li)$	Refs.
CH_3	417; 530 *	446; 558 *	11, 12	s-Bu	455; 515	528	9, 17
C_2H_5	532	550	13, 14	t-Bu	420; 480	429; 496	18
C_2H_5	535	565	11	$n\text{-}C_5H_{11}$	548	569	13
iso-Pr	475; 510 **	530	9	$n\text{-}C_{12}H_{25}$	550	—	13
n-Bu	545; 550	—	15, 16	C_6H_5	421	429	11

*Monomer.
**Hexamer.

Table 3. The charge characteristics (q) and association energies (E_a) of methyl-lithium.

Method of calculation	CNDO/1 (Ref.19)	Non-empirical method (Ref.20)	Method of calculation	CNDO/1 (Ref.19	Non-empirical method (Ref.20)
	CH_3Li			$(CH_3Li)_4$	
q_C	−0.39	−0.58	q_C	−0.26	−0.97
q_{Li}	+0.53	+0.57	q_{Li}	+0.04	+0.61
			E_a, kcal $mole^{-1}$	112.5	110.5

Quantum-chemical calculations on the CH_3Li and $(CH_3Li)_4$ molecules, carried out by the semi-empirical CNDO/1 method[19] and the non-empirical method[20], indicate a considerable energy gain on formation of aggregates. On the other hand, conclusions concerning the change in the polarity of the C–Li bond, which follow from the data of Cowley and White[19] and Guest et al.[20] do not agree (Table 3).

2. Complexes of Lithium Alkyls with Electron Donors

It follows from NMR and osmometric data[3,4] that lithium alkyls are tetrameric in polar solvents [diethyl ether, tetrahydrofuran (THF), and trimethylamine]. It has been suggested[8,21] that the hexamer is converted into the tetramer already for the molar ratio ED : $(RLi)_6 \simeq 1{-}2$. Intermolecular exchange can proceed as follows:

$$(RLi)_4.nED \rightleftharpoons 2(RLi)_2.n/2\,ED.$$

The existence of the monomeric form RLi, which follows from kinetic polymerisation data[5], could not be demonstrated with the aid of the above methods.

The NMR spectra of $(CH_3Li)_4$–polar solvent systems[3,4] indicate the occurrence of spin–spin splitting due to the $Li{-}^{13}C$ bond, which is evidence for an appreciable contribution of the covalent component to the C–Li bond. On the other hand, a significant spin–spin $^6Li{-}^7Li$ splitting is not observed, whence it follows that there is no bond between lithium atoms, i.e. that the aggregation effect is caused by the formation of Li–C–Li bridge bonds. It has

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‡According to theoretical considerations[10], the difference between the chemical shifts of the tetramer and the hexamer should be 0.1 p.p.m. Nevertheless the ^7Li NMR method does not permit the detection of the above forms of the iso-PrLi.

been established for the BuLi–THF system in a hydrocarbon medium[8] that there is no change in the ^{7}Li chemical shift in the range of THF : BuLi ratios from 1 to 14. This can be accounted for either by the formation of the complex $(BuLi)_4.4\,THF$ when the component ratio is only unity or by the impossibility of detecting separately the chemical shifts of various intermediate aggregates owing to the rapid intermolecular exchange even at –100° C. The NMR method has also been used to characterise qualitatively the formation of BuLi complexes with dioxan, dimethoxymethane, and tetrahydropyran[22].

Table 4. The stretching vibration frequencies of n-BuLi complexes of electron donors (cm^{-1}).

$(BuLi)_6$	T.ED	T.2ED	T.3ED	T.4ED	BuLi in THF
550	535—537	530	512—525	504	500

Table 5. The spectroscopic characteristics of electron donors and their complexes with n-butyl-lithium (cm^{-1}).

Electron donor	Absorption frequency				Refs.
	C–O–C stretching vibrations				
	symmetrical		asymmetrical		
	free	bound	free	bound	
DME	924	920	1096	1087	24
DEE	846	—	1120	1097	27, 28
DEE	837	—	1153	—	27, 28
DEE	—	—	1075	1068	27, 28
Ethyl methyl ether (EME)	855	—	1122	1097 (T.ED)	27, 28
EME	—	—	—	1099 (T.4ED)	27, 28
EME	843	—	1070	1070	27, 28
DBE	898	893	1120	1075	16
THF	912	898	1074	1050	24
Dimethoxyethane	850	—	1115	1100—1105	27
d,l-DMB*	848	900	1080	1050	26
d,l-DMB*	—	—	1105	1095	26
d,l-DMB*	—	—	1116	—	26
meso-DMB*	848	865	1085	1076	26
meso-DMB*	894	900	1122	1110	26
meso-DMB*	972	—	—	1085 **	26
Dimethoxymethane (DMM)***	927	927 (A);	1045	1030 (A);	29
DMM***	—	915 (B)	—	1027 (B);	29
	CH_2 stretching vibrations				
	free		bound		
DMM	1108		1105 (A); 1096 (B)		29
DMM	1138		1138 (A); 1131 (B)		29
	C–N bond stretching vibrations				
Trimethylamine (TMA)	828		822		30
Triethylamine (TEA)	1073		1064		30

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*Vinogradova et al.[26] used more carefully separated DMB stereoisomers than in the work of Kalnin'sh et al.,[16] which is the reason for the difference between the two sets of data.

**The above band is manifested for the ratio Li : ED = 8 with the simultaneous disappearance of the 1076 and 1110 cm^{-1} bands. The tentative composition of the corresponding complex is DMB. 2T.

***Here (A) is the monodentate complex T.4DMM and (B) is the bidentate complex T.2DMM.

The enthalpy of formation of the BuLi complex with diethyl ether (DEE) was estimated by gas–liquid chromatography (GLC)[23]; the value –5 ± 0.5 kcal mole^{-1} was obtained for the complex $(BuLi)_6.DEE$.

Table 6. Thermodynamic characteristics of the BuLi–electron donor systems obtained by the infrared spectroscopic method.

ED	*t*, °C	K_c, litre mole^{-1}*	$-\Delta H$, kcal mole^{-1}	Refs.	ED	*t*, °C	K_c, litre mole^{-1}*	$-\Delta H$, kcal mole^{-1}	Refs.
THF	30	8 (K_4)	5 ± 2	24	TMA	—20	40 ± 20 (K_2)	4 ± 0.5 **	30
EME	0	1 (litre mole^{-1})^2**	7 ± 2	28	TEA	—20	3.5+1 (K_2)	4 ± 1	30
DMM	0	5 (K_4)	4 ± 1.5	29					

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*See Eqns. (3) and (4).

**The quantity quoted corresponds to the case where $T.2ED \xrightarrow{2ED} T.4ED$.

Zgonnik and coworkers[16,24-26], who used the infrared spectroscopic method, showed in relation to dimethyl (DME), diethyl, and dibutyl (DBE) ethers, THF, and 2,3-dimethoxybutane (DMB) that the formation of a complex with BuLi entails bathochromic shifts of the ν(C–Li) and ν(C–O–C) bands. Systems with participation of DME and THF were studied in greatest detail[24]. It was established that the complexes are formed stepwise via n-butyl-lithium tetramers (T), differing in the degree of solvation:

$$2\,(BuLi)_6 + 3ED \overset{K_1}{\rightleftarrows} 3\,T \cdot ED,\quad T \cdot ED + ED \overset{K_2}{\rightleftarrows} T \cdot 2ED, \qquad (3)$$

$$T \cdot 2ED + ED \overset{K_3}{\rightleftarrows} T \cdot 3ED,\quad T \cdot 3ED + ED \overset{K_4}{\rightleftarrows} T \cdot 4ED. \qquad (4)$$

The values of ν(C–Li) corresponding to the products of these reactions are listed in Table 4. The first two ED molecules are linked to T very strongly, which follows from the almost complete absence of changes in the infrared spectra as the temperature is altered for complexes formed for the initial ratios THF : BuLi = 0.25 and 0.5.

The spectroscopic characteristics of a number of electron donors, both free and bound in complexes with BuLi, are listed in Table 5. The complex formation constants K_c and the enthalpies of complex formation were calculated from the absorption band intensities associated with the free and bound electron donors in some of the systems (Table 6).

The results presented in Tables 5 and 6 may be supplemented by the following comments. The preferential transformation of the *trans*, *trans*- and *trans*-conformations of the free electron donors into the *trans*,*gauche*-, and *gauche*-conformations on formation of the complexes of the electron donor with BuLi was demonstrated for DEE and MEE[27,28]. The maximum coordination saturation of lithium is rather difficult to achieve in the case of DEE and MEE; the complex corresponding to the composition T.4ED is formed to only an insignificant extent in the case of DEE even at –95° C.[28] The type of the complex of BuLi with DMM (Table 5) is determined by the temperature for a constant reactant ratio or by the DMM : BuLi ratio for a constant temperature. In particular, an increase of the BuLi concentration and a decrease of temperature promote the formation of the complex (B). The energy of the (B) ⇌ (A) transition is 12 ± 1 kcal mole^{-1}.[29]

The values of K_c could be estimated in only a limited number of cases, but the results permit the conclusion, the same as the familiar conclusions in the literature[31,32], that there is no simple relation between the physicochemical properties of the electron donors and their capacity for complex formation. Thus a number of data[16,24-29] make it possible to arrange the electron donors investigated in terms of the following activity series relative to BuLi as regards the relative amounts of the free and bound electron donors: DMB ≃ THF > DMM > DME > DEE > DBE. Since it does not agree with the variation of the ionisation potential I_p§, the steric structure of the electron donor and the number of heteroatoms may be regarded as the principal factors which determine the stability of the complexes. Data characterising the BuLi–NR_3 and BuLi–tetramethylethylenediamine (TMED) systems lead to an analogous conclusion. Thus I_p for trimethylamine (TMA) is higher than for triethylamine (TEA) (7.82 and 7.67 eV respectively[30]), but the former donor forms in the temperature range from −70° to −100°C appreciable amounts of the T.4ED complex, while the latter has been found to form only the T.ED and T.2ED complexes[30].

The complexes formed by BuLi with TMED, investigated for the first time by Langer[33,34], are known to be highly stable. In the reports quoted above, the determination of the infrared and NMR spectra of the complexes is mentioned, but no experimental results are given. The data of Zgonnik and coworkers[25], characterising the infrared spectra of the same system, indicate stepwise complex formation. Depending on the initial reactant ratio, complexes of the type T.*n*TMED, where *n* varies from 1 to 4, are formed; they are hardly dissociated and their composition is insensitive to changes in temperature between −30°C and 25°C.

The complexes of BuLi with another bidentate donor, namely DMB, whose *meso*-form has been studied[26], are much less stable. The limiting stoichiometry of the complexes in this instance also corresponds to the formula T.4ED, but, for an initial 1 : 1 reactant ratio (at 20°C in a hydrocarbon medium) there is an equilibrium between the free and bound molecules. The infrared spectra of this system, obtained in the presence of an excess of BuLi at −30°C, indicate the coexistence under the above conditions of the mono- and bi-dentate complexes. The characteristics of the $(BuLi)_4.n$ED complexes, obtained by the ^{1}H NMR method[35] at 20°C in iso-octane, are listed below (Δ is the chemical shift of the α-CH_2 group in BuLi):

ED	*n*	Δ, p.p.m.	K_C, litre mole^{-1}
DME	4	0.21	8 ± 2
DEE	3	0.14	6 ± 2
TEA	3	0.19	5 ± 2
DES	2—3	0.10	1

Comparison of the relative activities of several electron donors with different heteroatoms, including diethyl sulphide (DES), led to the following activity series: DME > DEE > DEA > DES.[35]

The formation of mixed complexes of electron donors with BuLi has been demonstrated for TMA and THF.[30] For the initial ratios BuLi : THF : TMA = 1 : 1 : 1 (in iso-octane as the solvent) and at −100°C, the complex includes approximately four times more THF than DMA; with increase of temperature, the DMA content rises somewhat.

Infrared spectroscopic data for systems with TMA, MEE, and THF also indicate the conversion of the complexes T.2ED in the range between −70° and −100°C into the complexes T.4ED (an absorption appears at 504 cm^{-1}; see Table 4). The absorption in the high-frequency region observed under these conditions (Fig. 2) led to the hypothesis[9,30] that the observed effects are due to the disproportionation of the complexes T.2ED, one of the products of which is the complex of the BuLi hexamer with ED. It is quite possible that the formation of the solvated hexamer compensates the energy gain accompanying the dissociation of the complex of the butyl-lithium tetramer.

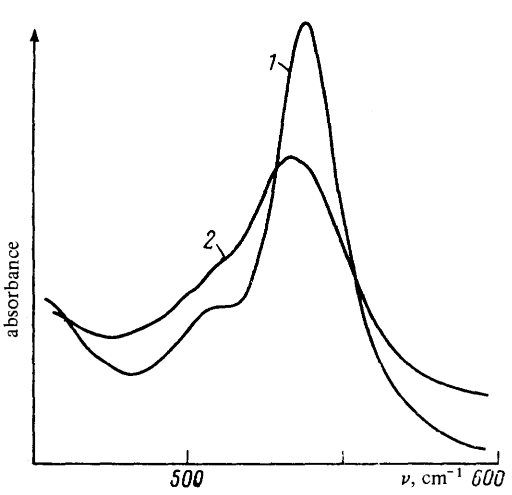
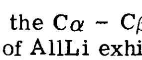


Figure 2. Infrared spectra of the 2.36 : 1 n-butyl-lithium–TMA-complex in iso-octane[30] at −17°C (curve *1*) and −100°C (curve *2*).

3. Allyl Compounds of Alkali Metals and Magnesium

The allyl derivatives of alkali metals are soluble only in electron-donating solvents or in a hydrocarbon medium containing an electron donor[36]. According to spectroscopic data (mainly NMR), under these conditions the C–Li bond in allyl-lithium (AllLi) is ionic at room temperature[36-39] and the allyl group has the delocalised structure



(I)

with free rotation about the Cα – Cβ and Cβ – Cγ bonds[36,37]. The infrared spectrum of AllLi exhibits a ν(C–C) = 1535 cm^{-1} absorption, which is characteristic of a delocalised structure with sp^2 hybridisation of the α-carbon atom[40]. Analogous data for the AllLi structure have been obtained[6] by ^{13}C NMR. According to Dolinskaya's data[36] for DME and West's data[39] for DEE and THF, the ^{1}H NMR spectra of AllLi at approximately −90°C demonstrate the presence of two types of terminal protons, which is a consequence of the complete inhibition of rotation about the above bonds. In asymmetric allyl derivatives, where the degree of delocalisation is reduced, the rotation about the

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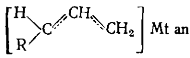
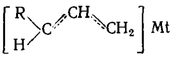
§THF has a smaller ionisation potential than DME, but, within the limits of the DME–DBE series, I_p decreases from 10.00 to 9.59 eV.[28]

Cβ–Cγ bond is already inhibited close to room temperature[36,39]. In a study of the vibrational spectra of the allyl compounds of lithium, sodium, and potassium, Lanpher[40] demonstrated the presence of two absorption bands corresponding to the following structures (where Mt is the metal):

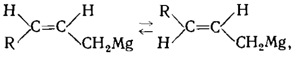


and



(II) (III)

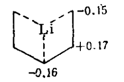
[In particular, the 1525 and 1560 cm^{-1} bands correspond to the pentenylsodium structures (**II**) and (**III**) respectively]. On the other hand, only one band is characteristic of the symmetrical derivatives (for example at 1520 cm^{-1} for 2-methylallylsodium). The allyl derivatives of magnesium exist at room temperature in an ethereal medium in the form of the equilibrium system



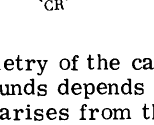
and with increase of the bulk of the substituent the fraction of the *cis*-isomer diminishes[41,42].

Among the quantum-chemical calculations for allyl compounds, the greatest interest attaches to AllLi data obtained by the non-empirical method[43]. According to these results, the symmetrical π-allyl structure with charges of −0.197*e* at the α- and γ-carbon atoms, −0.063*e* at the β-carbon atom, and +0.159*e* at the lithium atom, is energetically most favourable. Calculations for the model complex AllLi.2H₂O confirm the conclusion that the delocalised structure of allyl-lithium has the highest stability. Comparison of the AllLi dimerisation energy with the energies of formation of AllLi complexes with electron donors permit the conclusion that the formation of associated forms is favourable only in non-polar media.

The CNDO/2 semi-empirical method has been used in calculations on the $CH_2{=}CH{-}CH{=}CH{-}CH_2Li$ molecules with limited optimisation within the limits of several possible conformations[44]. The symmetrical structure illustrated below in a simplified form proved to be preferable:

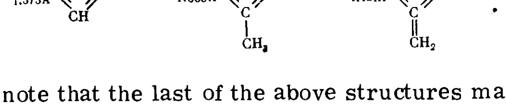


The same method has been used[45] in calculations on models of the terminal units of growing butadiene and isoprene chains associated with lithium counterions. The limiting *cis*- and *trans*-structures in their π- and σ-forms were compared. The most stable of these are structures of the type



R = H or CH₃.

The idea that the geometry of the carbanionic components of analogous compounds depends on the intrinsic structure of the alkenyls arises from the results of calculations on free allylic anions (the MINDO/3 method)[46]:



We may note that the last of the above structures may be adopted as the model of the fragment of the terminal unit in "living" buta-1,2-diene chains.

Sourisseau et al.,[38] who investigated the solid allyl compounds of lithium, sodium, and potassium by infrared spectroscopy, concluded that the allyl group has an ionic structure, which differs from its structure in π-allyl complexes of transition metals[47,48] and in covalent compounds of the type of allylmercury[49,50]. The assignments of the principal absorption bands of allyl derivatives of solid non-transition metals are listed below[38]:

Frequency, cm^{-1}	600	740	1000—1240	1400; 1460	1530	2900—3100
Assignment	δ (CCC)	r_0 (CH_2)	δ (CH); ν_s (CCC)	δ (CH_2)	ν_{as}(CCC)	ν (CH); ν (CH_2)

A set of bands in the broad range 100–600 cm^{-1} is characteristic of the C–metal bond; their multiplicity is attributed to the polymeric structure of the compounds. The force constants of the C–metal bond in the allyl compounds were found to be 0.31, 0.44, 0.55, and 0.80 mdyn $Å^{-1}$ for sodium, lithium, potassium, and magnesium derivatives respectively[38,46]. It follows from the above quantities that the bond is less stable than the C–metal bond in the analogous alkyl derivatives; thus the force constants of the C–Li bond in CH₃Li is 0.78 mdyn $Å^{-1}$.[12]

The infrared spectra of ethereal solutions of allyl compounds of lithium and magnesium contain, instead of the 600 cm^{-1} band (characteristic of the compounds in the solid state), two bands at 580 and 630 cm^{-1}, which have been attributed[38] to the effect of association. The infrared spectrum of a crotylmagnesium derivative, obtained from butadiene and magnesium in THF[51], contains bands at 1590 and 1615 cm^{-1} in the region of the ν(C=C vibrations), which the authors assigned to complexes with THF differing only in the degree of solvation (noting, however, that distillation of THF does not entail changes in the infrared spectrum of the system)[51].

The estimates of the dependence of the relative C–metal bond strengths on the nature of the substituent, carried out for alkyl and alkenyl derivatives of lithium[52], merit attention. The estimates were based on the enthalpy of alcoholysis (Δ*H*) of the etherates of various compounds RLi. The results, in the calculation of which account was taken of the degree of association of the initial compounds and of solvation effects, indicate a reduced strength of the bond in 2-propenyl lithium compared with other compounds investigated:

R	ethyl	allyl	*trans*-propenyl	2-propenyl
Δ*H*, kcal $mole^{-1}$	−7.1±1.3	4.3±1.3	5.4±0.5	20.1±2.8

III. "LIVING" POLYMERS

1. Non-polar Chains with a Lithium Counterion

In order to investigate systems simulating the active centres in the anionic polymerisation of non-polar monomers, use is frequently made of the NMR method, which makes it possible to obtain information about the structure of the terminal unit, the distribution of charges in the latter, and the type of the C–lithium bond. Low-molecular-weight adducts, formed when diene monomers (M) and s- or t-butyl-lithium interact in the proportions M : BuLi ≃ 1, have been studied as models of this kind. In order to eliminate the influence of preceding units, which complicate the NMR spectra, "living" oligomers, containing deuterated monomeric units in the main chain and a non-deuterated terminal unit, were used in a number of studies[53–56].

It follows from the chemical shifts of the α- and γ-protons of the $\sim \overset{\delta}{C}H_2-\overset{\gamma}{C}H=\overset{\beta}{C}H-\overset{\alpha}{C}H_2Li$ unit that in non-polar media most of the charge is at the α-carbon atom with a proportion of the negative charge at the γ-carbon atom. In a polar medium an upfield shift of the γ-H signal and a downfield shift of the α-H signal are observed, which indicates an increase of electron density at the γ-carbon atom. In a study of the NMR spectra of alkenyl compounds of lithium Bywater et al.[6] showed that in the THF the allyl group of allyl-lithium has the structure of a symmetrical anion with sp^2 hybridisation. It follows from the data for crotyl-lithium that the introduction of a substituent causes the breakdown of the symmetry of the anion with retention of the type of hybridisation. The chemical shifts of the α- and γ-carbon atoms in the ^{13}C spectrum of crotyl-lithium differ from the corresponding values for allyl-lithium by −14.7 and +18.7 p.p.m. An analogous effect was observed for models of "living" chains with terminal butadiene and isoprene units, which consisted of the adducts of t-BuLi with the corresponding monomers. These adducts were investigated in a non-polar medium which led to an appreciable alteration of the nature of hybridisation, namely from sp^2 to sp^3. In particular, the butadienyl derivative contains only approximately 1/3 of the charge at the γ-carbon atom relative to the charge at the γ-carbon atom of allyl-lithium.

Table 7. The ^1H NMR chemical shifts (Δ) in the model compounds RM_nLi obtained by reaction with t-BuLi.

M	n	t, °C	Solvent	Δ, p.p.m.			Refs.
				α-CH₂		γ-CH	
Butadiene	1.2	20	methylcyclohexane–THF (1:1	*cis*	1.09	3.40	56
				trans	1.18	3.68	
Butadiene	1	30	toluene-d_8	*cis*	0.811	4.50	57
				trans	0.775	4.64	
Butadiene	1	20	benzene-d_6		0.6	4.6	56
Butadiene	1	30	THF-d_8	*cis*	1.19	3.35	57
				trans	1.29	3.63	
Butadiene	1	0	THF-d_8		1.2	3.5	56
Butadiene	1	20	THF-d_8	*cis*	1.1	3.0	53,*
				trans	1.2	—	
Butadiene	3—4	20	benzene-d_6		1.25	4.55	36
Butadiene	3—4	20	DME		1.20	3.0—3.75	36
Isoprene**	1	25	benzene-d_6		619	236	58
	1	0	THF		631	403	
	1	60	THF		621	363	
Isoprene	5	20	benzene-d_6		0.45	4.8	54
2-Ethylbutadiene	1	20	benzene-d_6	*cis*	—	4.72 ***	59
				trans	—	4.55 ***	
Phenylbutadiene	1	20	benzene-d_6	*cis*	0.5—2	4.70	59
				trans	—	4.95	
2,3-Dimethylbutadiene	1	20	benzene-d_6	*cis*	0.8	—	36
cis-Penta-1,3-diene	1	20	benzene		2.9	5.5	36
			benzene + DEE		4.0	3.9	
trans-Penta-1,3-diene	2.7	20	benzene-d_6		—	3.1 ****	55
					—	4.6	
2-Methylpenta-1,3-diene	1	20	benzene-d_6	*cis*	0.8	4.6	59
				trans	—	4.3	
Hexa-2,4-diene	2.2	20	benzene-d_6		—	3.1	55 *****

*Initiator—deuterated ethyl-lithium.

**The chemical shifts are quoted relative to benzene.

***Triplets.

****Initiator—isopropyl-lithium.

*****Initiator—s-BuLi.

The principal results of Bywater et al.[6] are listed below [$\Delta = \delta_{RH} - \delta_{RLi}$ (p.p.m.) is the difference between the chemical shifts]:

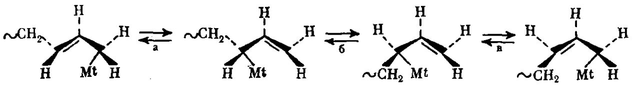
R	Solvent	Δ, p.p.m.		
		α-C	β-C	γ-C
$CH_2{=}CH{-}CH_2$	THF	31.7	13.6	—64.8
$CH_3CH{=}CH{-}CH_2$	THF	17.0	19.5	—46.1
$(CH_3)_3CCH_2CH{=}CH{-}CH_2$	C_6H_6	5.3	16.2	—25.2
$(CH_3)_3CCH_2CH{=}C(CH_3){-}CH_2$	C_6H_6	3.9	17.2	—21.6

A compilation of ^1H NMR data characterising the chemical shifts of the protons attached to the α- and γ-carbon atoms in low-molecular-weight organolithium compounds with terminal units consisting of diene monomers is presented in Tables 7 and 8. Despite the abundance of such data, there is no unanimous view in the literature concerning the type and state of the terminal unit. Nevertheless the conclusion that it has the 1,4-structure (or the 4,1-structure for isoprene) with limited rotation about the Cβ − Cγ bond, responsible for the coexistence of the *cis*- and *trans*-isomers, is fairly general. In a polar medium (in contrast to a non-polar medium) the *cis*- and *trans*-structures are in equilibrium and, as shown for butadiene[60] and isoprene[58,61] isomers, the *cis*-structure predominates at approximately −70°C.

Table 8. ^1H NMR chemical shifts (Δ) in the model compounds $RM_nM'_mLi$ obtained by reaction with C_2D_5Li (measurements in benzene-d_6 at 20°C).

M	n	M′	m	Δ, p.p.m.		Refs.
				α-CH₂	γ-CH	
Butadiene-d_6	20	butadiene-H_6	2.4	0.8	4.75	53
Butadiene-d_6	20	isoprene-H_8	8.8	0.87	4.75	54
Butadiene-d_6	20	2,3-dimethylbutadiene-H_{10}	2	0.7	—	54

Morton and Fetters[62] assume the existence in a non-polar medium of two types of active centres of dienyl (living) chains—a localised centre (with a C–lithium σ bond), responsible for the formation of the 1,4-units, and a delocalised centre giving rise to 1,2-units. There is no direct evidence for the presence of the π-allyl structure of agents of this kind in non-polar media. Nevertheless, according to Morton and Fetters, the content of vinyl units in the chains of the corresponding diene polymers may be regarded as an indirect indication of the presence of active centres of the σ-allyl types in numbers undetectable by NMR. According to this view, the *cis–trans* isomerisation proceeds via the structure $\sim CH_2{-}\overset{3}{C}H(Li)\overset{2}{C}H{=}\overset{1}{C}H_2$ in which there is free rotation about the $C_{(2)} - C_{(3)}$ bond. Morton and Fetters base their hypothesis on the nature of the ^1H NMR spectra of oligopentadienyl-lithium (OPL) in benzene[55], attribute the chemical shift of 3.1 p.p.m to the γ-proton (Table 7), and conclude (by analogy with data for oligobutadienyl-lithium in THF) that the terminal OPL unit has a π-allyl type of structure; the chemical shift of the α-proton is not quoted. Dolinskaya[36], who found chemical shifts of 2.9 and 5.5 p.p.m. for the α- and γ-protons of *cis*-OPL in benzene respectively, concluded that a different isomerisation mechanism operates, namely that the reaction proceeds via the delocalised structure (I) with free rotation about the Cβ – Cγ bond (see above); this structure is consistent with data which she obtained[36] for the change in the chemical shifts of OPL on passing from a non-polar to a polar medium (Table 7). Glaze and coworkers[63,64] postulate the possibility of the oscillation of the metal atom between two potential minima for each geometrical isomer (equilibria *a* and *c*); isomerisation (equilibrium *b*) is significant only for magnesium derivatives at an elevated temperature:



We may note that all the results quoted for non-polar media refer to associated lithium alkenyls. The monomeric forms $RM_nLi.ED$ are apparently formed in polar media. As regards their nature, they should differ appreciably from the monomeric forms RM_nLi, which, according to generally accepted views, are the most active species in the polymerisation of unsaturated monomers in a hydrocarbon medium.

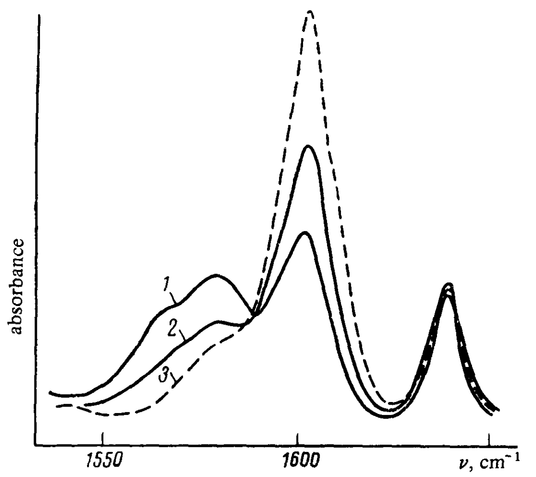


Figure 3. Infrared spectra of an artificial 1 : 1 OBL–s-BuLi mixture (curves *1* and *2*) and OBL (curve *3*) in iso-octane[17] at different temperatures (°C): 1) –31; 2) –1.5; 3) –31.

Glaze and Jones[65] were the first to use the infrared spectroscopic method in the study of compounds simulating the active centres in anionic polymerisation. The authors observed absorption bands at 1597 and 1577 cm^{-1} in the infrared spectrum of the product of the interaction of t-BuLi with butadiene and assigned them to the vibrations of the C=C bonds of the terminal units in the *cis*- and *trans*-structures respectively. These studies were developed further by Basova and coworkers[66–68] and Zgonnik and coworkers[69–71]. In particular, a detailed study of oligobutadienyl-lithium (OBL), obtained by reaction with s-BuLi, revealed a dependence of the 1602 and 1580 cm^{-1} absorption bands on the initial monomer : initiator ratio and temperature. It follows from the analysis of the infrared spectra of artificial mixtures of the initiator and OBL that the latter band refers to mixed associated species $(OBL)_3.BuLi$ (Fig. 3).

Infrared spectroscopy was then used for a more detailed investigation of OBL and was extended to the study of other "living" chains with the lithium counterion[67–76]. Zgonnik et al.[69–71] made the most complete assignment of the absorption bands in the infrared spectrum of OBL, based on the isotopic substitution of ^7Li by a ^6Li and selective deuteration of butadiene. The characteristics of the terminal unit of OBL and its deutero-analogues in the range 400–1200 cm^{-1}, presented in Table 9, demonstrate a significant contribution of the deformation vibrations of the α-CH_2 group to the 600, 775, 850, and 940 cm^{-1} bands. The isotopic shift factor for the majority of bands in the infrared spectra of the deutero-derivatives does not exceed 1.2, indicating an appreciable mixing of the vibrations of the α-CH_2 and =CH groups, which makes the out-of-plane =CH vibrations in the terminal units less characteristic. It appears that the 895 and 695 cm^{-1} bands in the spectra of OBL and OBL-d_6 respectively refer to the *trans*-structure of the terminal unit.

Table 9. The assignment of the principal absorption bands (cm^{-1}) in the infrared spectra of oligobutadienyl-lithium (OBL) and its deuterated derivatives (OBL-d_n).[71]

C—Li	α=CH_2	α-CH_2+ =CH	=CH	C—Li	α-CH_2	α=CH_2+ =CH	=CH
	OBL				OBL-d_4(1,1′, 4,4′)		
430 m. 482 m.	600 s.	775 s.	895 s.	427 m. 475 m.	525 s.	670 s.	817 m.
	OBL-d_2(2,3)				OBL-d_6		
425 m. 475 m.	582 s. 850 m.	758 s.	770 sh.	425 m. 475 m.	515 s. 766 w.	633 s.	695 s.

Note. s = strong (intense) absorption band, m. = moderately intense band, w. = weak band, sh. = shoulder.

The stretching vibration band of the double bond in the terminal unit is sensitive to the type of deuteration:

Compound	OBL-H_6	OBL-d_2 (2,3)	OBL-d_4 (1,1′, 4,4′)	OBL-d_6
$\nu_{C=C}$, cm^{-1}	1602	1568	1594	1564

It is a single band (only a slight shoulder was noted at 1580 cm^{-1})¶, which indicates the preferential existence of a structure of one type. The direction of the shift on deuteration is consistent with the NMR data and the 1,4-structure of the terminal unit.

Oligoisoprenyl-lithium (OIL)[72,73] and oligo-2,3-dimethylbutadienyl-lithium (ODMBL)[75] were investigated similarly. The frequencies (cm^{-1}) of the absorption bands of the terminal OIL and ODMBL units (in iso-octane) are listed below:

Compound	C—Li	$=C<^{H}_{C}$; $=C<^{C}_{C}$	α-CH_2	C=C	References
OIL	455,475	575	600	1600	72
OIL-d_4 (1,1′, 4,4′)	455,475	500	540	1600	73
ODMBL	445,495	560	595	1600	74,75

¶This shoulder may, in principle, refer to another structure of the terminal unit responsible for the formation of 1,2-units in the polymer; its contribution does not exceed 10%.

We may note that the low-frequency shoulder characteristic of OBL is absent from the spectra of OIL and ODMBL, indicating a more homogeneous structure of the terminal units of OIL and ODMBL, which evidently have the *trans*-4,1-structure.

Table 10. The NMR characteristics of the terminal units of the "living" chains of styrene and α-methylstyrene with a lithium counterion.

Compound	Solvents (deuterated)	Chemical shifts of signals due to protons at C atoms, p.p.m.			Charges on ring C atoms			Refs.
		o-	*m*-	*p*-	*o*-	*m*-	*p*-	
OStL	benzene	5.98	6.53	5.52	—0.11	—0.06	—0.16	77
OStL	THF	5.87	6.32	5.12	—0.12	—0.08	—0.19	
OMStL	benzene	5.67	6.23	4.66	—0.16	—0.09	—0.24	77
OMStL	THF	5.57	6.10	4.46	—0.17	—0.10	—0.26	
OMStL*	benzene	109.4	129.0	97	—0.13	—0.01	—0.19	6

*The chemical shifts of the signals due to the ^{13}C nuclei.

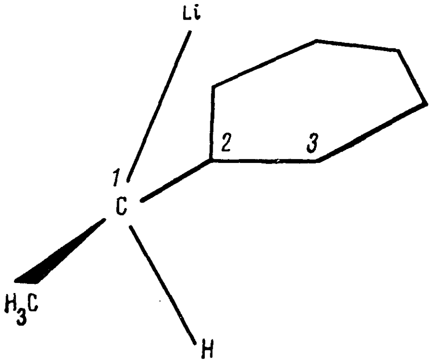
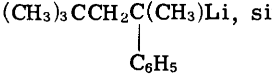


Figure 4. The optimised geometry of the model active centre $CH_3CH(Li)C_6H_5$.[80] Li–C distance (Å): 1) 2.1; 2) 2.2; 3) 2.2.

Different spectroscopic characteristics have been obtained for oligostyryl- and oligo-α-methylstyryl-lithium (OStL) and (OMStL). The ^{1}H NMR spectra led to the conclusion that at least half of the charge of the anionic component is concentrated on the benzene ring[6,77–79], the fraction of this charge increasing on passing from benzene solution to THF solution (Table 10). A paper[76] dealing with the infrared spectra of OStL lists the following characteristics of the terminal unit:

ν, cm^{-1}	505	1585	2800
assignment	δ (Li—CH)	in-plane C_6H_5 vibrations	ν(C-H) vibrations of CHLi

The appreciable difference between the intensity of the 1585 cm^{-1} absorption band of the terminal unit of OStL and the data for the internal units (by a factor of approximately 10) indicates the interaction of the terminal benzene ring with the counterion. This conclusion is consistent with the results of a quantum-chemical calculation on the $CH_3CH(Li)C_6H_5$ model compound by the CNDO/2 method[80], according to which the lithium atom in the optimised structure is significantly closer to the C_6H_5 group (Fig. 4); see also below.

Wicke and Elgert[81] arrived at a similar conclusion in a study of the ^{13}C NMR spectra of the compound  $(CH_3)_3CCH_2\underset{\displaystyle C_6H_5}{\underset{|}{C}}(CH_3)Li$, simulating the terminal unit of the growing chain of α-methylstyrene. The orientation of the lithium atom relative to the benzene ring which they propose[81] agrees in principle with the geometry illustrated in Fig. 4.

2. Complexes of the Compounds RM_nLi with Electron Donors

The results of studies on the interaction of "living" hydrocarbon chains with small amounts of electron donors in non-polar media are considered in this section. Under such conditions, monodentate donors do not cause the decomposition of associated groups of "living" chains on formation of compounds of different stoichiometries. Thus, according to isothermal distillation and conductimetric data[82], the reaction of oligobutadienyl-lithium tetramer (T) with THF in iso-octane results in the formation of the complexes T.4THF and T.8THF at room temperature. Measurements of the electrical conductivity of the second complex showed that its ionic dissociation constant is 10^{-13} mole litre^{-1}. Data for the dielectric constants of the OBL tetramer and its complexes yielded the following dipole moments:

Compound	T	T.4THF	T.8THF
μ, D	4.0	7.7	10.4

Such high constants indicate the asymmetry of the OBL tetramer, which becomes more pronounced in its complexes.

A large amount of information has been obtained in studies of the mechanism of the formation of complexes between "living" oligomers and electron donors by infrared spectroscopy[67–76,83]. For ED/Li ratios ensuring the formation of 1 : 1 complexes with DME,[69] DMM,[83] and THF,[69–71] the infrared spectra in the region of the stretching vibrations of the C=C band of the terminal units are virtually identical: the 1600 cm^{-1} absorption band is displaced in steps to 1570 cm^{-1} as the electron donor concentration is increased. Qualitatively analogous effects have been described in other studies[67,68] devoted to the formation of complexes by polybutadienyl-lithium with THF and TEA. Such a shift corresponds to transitions of the type

$$T \underset{}{\overset{ED(K_1)}{\rightleftarrows}} T.ED \overset{ED(K_2)}{\rightleftarrows} T.2ED \overset{ED(K_3)}{\rightleftarrows} T.3ED \overset{ЭД(K_4)}{\rightleftarrows} T.4ED, \qquad (5)$$

and $K_1 > K_2 > K_3 > K_4$. The bathochromic shift of the ν(C=C) band is apparently caused by the partial delocalisation of the double bond on formation of a complex by the counterion of the "living" chain with the electron donor. The 1570 cm^{-1} band may be fairly confidently assigned to the complex T.4ED. The overlapping of the bands characterising each individual complex has not so far permitted the determination of the individual constants K_1–K_4; only certain average values of the complex formation constants (K_C) have been estimated.

The spectroscopic and thermodynamic characteristics obtained for several systems of the type under consideration are listed in Table 11. We shall consider some of them in somewhat greater detail and will supplement them with data not included in Table 11. An increase of the ED :OBL ratio to 10 does not alter the nature of the infrared spectrum of DME and DMM, but does entail the appearance in the case of THF of a new band in the region of ν(C=C) (1555 cm^{-1}) and a sharp decrease of the intensity of the 450 cm^{-1} band associated with the C–Li bond[71]; these changes have been attributed to the decrease of the degree of association of OBL under the influence of the excess of THF. The decrease of temperature in the last of the systems indicated to –100°C results in the appearance of a new intense band (447 cm^{-1})[71] in the region of the stretching vibrations of the C–Li bond and of two extremely intense bands (550 and 607 cm^{-1}) in the region of the deformation vibrations of the C–H bond, instead of the previous relatively low-intensity band at 600 cm^{-1}. Such changes can be accounted for either by a rearrangement in the α-CH_2Li group due to association–dissociation steps[71] or, on the basis of data obtained by other methods (NMR[60], ultraviolet spectroscopy[85], and chemically[61]), in terms of the *cis–trans* transitions in the terminal unit.

Table 11. Complex formation in M_nLi–ED–non-polar solvent systems at 20°C.

M	ED	ED:Li	$\nu_{C=C}$, cm^{-1}	K_c, litre mole^{-1}	$-\Delta H$, kcal mole^{-1}	Refs.
Butadiene	DME	1	1570—1580 (1602) *	8 **	7 **	69
Butadiene	THF	1	1565—1580 (1602) *	20 **	9 **	70, 71
Butadiene	THF	10	1555—1580	—	—	70, 71
Butadiene	DMM	1	1570 (1602) *	3	3	83
Butadiene	TMED	1	1525, 1550	—	—	88
Isoprene	THF	1	1570 (1602) *	8.5	4	72
Isoprene	THF	30 ***	1575	—	—	72
Isoprene	Dimethoxyethane	1	1570	—	—	73
Isoprene	Dimethoxyethane	4	1590	3.5	5 ****	84
Isoprene	Dimethoxyethane	10	1530—1585	—	—	84
Isoprene	TMED	1	1570 *****	—	—	87
2,3-Dimethyl-butadiene	TMED	1	1528 (1582)	1.0	2.0	74
	TMED	4	1528 (1582)			
2,3-Dimethyl-butadiene	THF	1	1580 (1602) *	—	—	75

*The characteristics of the part of the "living" chain not bound in a complex.

**Values calculated from data in Refs. 69 and 70.

***THF used as reaction medium.

****Value corresponding to the complex OIL. 2ED.

*****Data refined after the publication of the paper of Davidyan et al.[84]

The formation of complexes between THF and OIL[72,73] is somewhat less vigorous than the reaction involving OBL. The stepwise bathochromic shift of ν(C=C) reaches a limit (1570 cm^{-1}) for an equimolar reactant ratio in the complex and remains unchanged up to the ratio ED :OIL = 10 in the reaction mixture. Only when THF is used as a solvent is a shift of the 1570 cm^{-1} band to 1575 cm^{-1} observed; the previous bands, due to the C–H bond, disappear and are replaced by a single intense absorption at 690 cm^{-1}. Monomeric complexes of the type OIL. *n*ED are apparently formed in THF; other workers[86], who investigated the analogous system by ultraviolet spectroscopy, arrived at the same conclusion.

Glyme, a bidentate electron donor, has a different effect on the terminal unit of OIL[84]. For the ratio glyme :OIL = 4 at a low temperature, unassociated complexes OIL. 2ED are already formed (the absence of association was demonstrated viscometrically). However, the frequency of the absorption band of the C=C bond in the terminal unit corresponding to these complexes is higher (1590 cm^{-1}) than in the case of complexes involving THF.

We shall now compare results referring to the formation of complexes by different oligodienyl-lithium derivatives with TMED. The simplest situation is observed for OIL[73,87]. For an initial reactant ratio of unity, the ν(C=C) band is displaced to 1570 cm^{-1}, which corresponds to a 1 :1 complex, an increase of the TMED concentration and a decrease of temperature not resulting in a shift of this band. Consequently, even for the equimolar ratio of OIL and TMED, a stable complex of a definite type (apparently monomeric) is formed. A similar conclusion is reached on the basis of the ultraviolet spectra of the same system; they are characterised by a single maximum at 330 nm, which is independent of temperature and the excess of TMED. The following absorption bands are characteristic of complexes of other oligodienyl-lithium complexes with TMED in the region of ν(C=C) vibrations: 1528 and 1550 cm^{-1} for OBL[88] and 1528 and 1582 cm^{-1} for ODMBL[74,75]. The first complex is very stable and its infrared spectra (as well as ultraviolet spectra; λ_{max} = 320 nm) are insensitive to the presence of an excess of TMED and a change of temperature. When the ratio TMED :Li = 1, complexes with the 1 :1 composition are formed and are present in solution in a monomeric form[88]. ODMBL exhibits a much lower capacity for complex formation. Analysis of the infrared spectra obtained for different TMED :ODMBL ratios (from 0.27 to 4.6) shows[74,75] that complete coordination saturation of the tetramer is not attained under the given conditions: only the formation of the complexes $(ODMBL)_4$.TMED and $(ODMBL)_2$.2TMED was observed.

According to the data described above, the stability of the complexes of the compounds considered and the electron donors decreases in the sequence OBL > OIL > ODMBL, probably primarily due to the steric structure of the electron acceptors.

The spectroscopic effects observed in the OStL–ED systems differ from those described for diene derivatives. A hypsochromic shift of the 1585 cm^{-1} band to 1590 cm^{-1} is characteristic of the benzene ring[76]. This result is probably due to the breakdown of the specific interaction between lithium on the aromatic ring (see above concerning the characteristics of the terminal unit of OStL). We may note that an analogous hypsochromic shift of the ν(C=C) band was observed[89] after the introduction of diethyl ether to a hydrocarbon solution of γ-butenyl-lithium, which forms an intramolecular π-complex in the absence of an electron donor.

Genkin and Moiseeva[90] investigated the stabilities of the complexes of OBL, OIL, and OPL with TMED, DEE, and di-isopropyl ether (DIPE) by GLC. K_1 was calculated [see Eqn. (5)], since, according to the conditions employed in the method the electron donor chromatographed is present at infinite dilution in relation to the oligomers. The characteristics obtained agree with the activity series of the electron acceptors (OBL > OIL > OPL) and donors (DME > DEE > DIPE). From the large number of quantities quoted by the above workers[90], we shall select only data for complexes of lithium alkenyls with DME:

Acceptor	OBL	OIL	OPL
K_1, litre mole^{-1} (20°C)	305	211	204
$-\Delta H$, kcal mole^{-1}	8.6	7.7	7.3

The study of the products of the deactivation of "living" oligomers of the diene series confirmed the 1,4(4,1)-structure of the terminal unit and showed that the fixation of the chain structure takes place in the propagation stage only in the penultimate unit[91-93]. Apart from the nature of the monomer and the solvent, the structure of the terminal unit is influenced also by the nature of the deactivating agent[93-95]; it has been suggested[93] that the chain termination reaction proceeds under these conditions via a complex formation stage.

3. Derivatives of Sodium, Potassium, and Magnesium

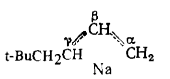
"Living" chains with a sodium counterion, with a limited solubility in hydrocarbons, have been investigated mainly in polar media. The electronic spectra indicate a much lower stability of such systems compared with the corresponding lithium derivatives[96], which is manifested in a number of irreversible reactions (the transfer of a hydride ion to the counterion[97], intramolecular proton transfer[98], the formation of alkoxides[99,100], and metallation of the solvent[101]). The *cis–trans* isomerisation of the terminal unit has also been noted[64,85]. Sodium derivatives of dienes in THF are less stable at room temperature than the corresponding derivatives of styrene[101,102], but in the region of low temperatures (–30° C), the opposite effect is observed[101,103]. These characteristics determine the temperature and time limits of the experimental study of the agents under consideration†.

Gourdenne and Sigwalt[103] showed that sodium-butadiene chains are more stable than the isoprene chains, but both undergo changes on being kept in THF (some of them reversible), which are manifested in the electronic spectra. Thus the 293 $\rightleftharpoons$ 384 → 435 and 308 $\rightleftharpoons$ 358 → 435 nm shifts of λ_{max} were observed for butadienyl and isoprenyl derivatives of sodium respectively‡. The terminal products of these reactions are inactive in relation to dienes.

The ^{1}H NMR chemical shifts (p.p.m.) in neopentylallyllithium (NPAL) and neopentylallylsodium (NPAS) are listed below (solvent—THF)[60,64]:

Compound	*cis*-Proton		*trans*-Proton		References
	α-C	γ-C	α-C	γ-C	
NPAS	1.52	2.85	—	3.55	64
NPAL	1.19	3.35	1.29	3.63	60

It follows from the data presented that NPAS is more ionic. The temperature at which the rotation about the Cβ – Cγ bond in the structure



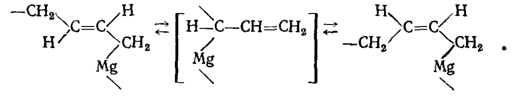
is inhibited (in terms of the NMR time scale) proved to be –20° C for NPAS and –55° C for NPAL, which indicates a higher Cα – Cβ bond order, i.e. a greater amount of ionic character of the C–Na bond compared with C–Li. The difference between the ultraviolet characteristics of NPAS and NPAL (λ_{max} = 293 and 278 nm respectively[60,63], conflicting with the hypothesis that the absorption maximum of the All–Mt contact ion pairs increases with the atomic number of the metal[104] and that absorption at longer wavelength is characteristic of more polar bonds, was explained by Glaze by the higher fraction of the *cis*-form in NPAS compared with NPAL; absorption in the region of shorter wavelengths is characteristic of the *cis*-form[100,101]. This conclusion was confirmed by the analysis of the corresponding hydrolysis products (Table 12). Garton and Bywater[85] explained the changes in the ultraviolet spectra of the polybutadienyl chains with lithium and sodium counterions after the introduction of the monomer at a low temperature (in THF) by the isomerisation of the terminal unit. The 285 and 336 nm absorption bands were assigned to the more stable *cis*-forms, while the 320 and 350 nm bands, arising after the introduction of the monomer, were assigned to the *trans*-forms of the lithium and sodium derivatives respectively.

Table 12. Structures of the hydrolysis products of the neopentylallyl derivatives of lithium, sodium, and magnesium (NPAM).

Compound	Solvent	Content of units, %			Refs.
		trans-1,4	*cis*-1,4	1,2	
NPAS	THF	27	54	20	64
NPAL	n-pentane	75	23	2	57
NPAL	DEE	68	21	11	60
NPAL	THF	49.4	36.9	13.7	
NPAM	n-pentane	42.7	19.2	38.1	63
	DEE	17.7	11.7	70.5	

The study of "living" chains with a potassium counterion is complicated by the still more intense irreversible changes which occur even at –70° C.[85] Basova and coworkers[67,68] studied polybutadienylsodium (PBS) and polybutadienylpotassium (PBP) in a hydrocarbon medium by infrared spectroscopy. In the region of the stretching vibrations of the terminal C–C bond, the following absorption bands were found (cm^{-1}): 1555 (main band) and 1535 and 1570 (shoulders) for PBS and 1570 (main band) and 1535 and 1555 (shoulders) for PBP. These characteristics indicate a greater degree of delocalisation of the above bond in PBS and PBP than in the lithium derivatives (see above). The authors attribute the 1555 cm^{-1} band in the spectrum of PBS to the presence of a certain amount of lithium alkoxide formed in the course of the synthesis[68] and interacting with the sodium counterion and assume that lithium alkoxide may not affect PBP owing to the low electron-accepting capacity of potassium[67,68].

The state of the terminal alkenyl unit with a magnesium counterion is described by a scheme[63] based on ^{1}H NMR data for a solution of neopentylallylmagnesium (NPAM) in THF at room temperature:



At a reduced temperature (~ –40° C) the attainment of equilibrium is retarded and the signals due to the *cis*- and

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† The references to earlier studies by Medvedev and coworkers, who considered these questions, are listed by Medvedev and Gantmakher[101].

‡ Data for –40° C; the "living" polymers were obtained under the influence of sodionaphthalene.

trans-isomers, present in comparable amounts, are distinguishable. The contents of units having different structures in the hydrolysis products of an ethereal solution of NPAM were 17.7, 11.7, and 70.5% for the *trans*-1,4-, *cis*-1,4-, and 1,2-units respectively. Consequently the conclusion that the content of the *cis*-units is reduced with decrease of the amount of ionic character of the C–Mt bond has been confirmed in this instance too. On the other hand, the content of the 1,2-units in NPAL, NPAS, and NPAM is not directly related to the electronic structure of the corresponding alkenyl units (Table 12).

4. Derivatives of Polar Monomers

The formation of "living" chains of the type M_nMt, where M is a polar monomer, is usually difficult owing to their lower stability compared with the hydrocarbon chains and the side reactions, which occur differentially in the initial stage of the synthesis[107]. Side reactions can be virtually eliminated by a procedure involving the interaction of the "living" hydrocarbon chains (for example, butadiene or styrene chains) and small amounts of polar monomers. When certain conditions are observed, this ensures the introduction into the non-polar chain of several terminal units of the polar monomer. This procedure has proved particularly useful for acrylonitrile (AN) and methacrylonitrile (MAN), whose polymers are soluble only in solvents which tend to interact irreversibly with organometallic compounds (dimethylformamide, dimethyl sulphoxide, etc.). The determination of the spectroscopic and electrochemical characteristics of the chains corresponding to these monomers is possible only for macromolecules containing a fairly long non-polar block. Some of the data of Tsvetanov and coworkers[108,109] for the electronic spectra and dissociation constants (K_d) of macromolecules of the above type, consisting of a butadiene block (40–50 units) and 2–3 terminal AN units, are presented below (25° C):

Solvent	Iso-octane		THF		
Mt	Li	Na	Li	Na	K
λ_{max}, nm	330.5	337.5	342	345	351
$10^9 K_d$, mole litre^{-1}	—	—	2.4	4.0	30.0

The infrared spectra of analogous substances with a styrene main block, recorded in benzene (20° C) and THF (−40° C)[110], indicate a significant difference between the absorption band due to the nitrile group of the –CH(CN)Mt fragment and the band characteristic of the usual nitriles, including polyacrylonitrile (PAN). Thus "living" chains with Li^+, Na^+, and K^+ counterions absorb in the range 2030–2040 cm^{-1}, while PAN absorbs at 2235 cm^{-1}. The first of the above bands refers to chains containing one AN unit. An increase in the number of such units leads to a hypsochromic shift of this band (particularly 2032 → 2040 and 2042 → 2049 cm^{-1} for chains with potassium and lithium counterions respectively) and to the appearance of new bands, including a band which virtually coincides with that observed in the spectrum for the unperturbed nitrile group (2235–2040 cm^{-1}).

The conclusion concerning the strong interaction of the counterion and the polar group of the macromolecule, which follows from these results, agrees with the finding in one of the studies quoted above[109] that there is no association between the chains and the lithium counterion in a hydrocarbon medium (this conclusion is based on viscometric data), which distinguishes them from organolithium compounds with non-polar constituents. Strong intramolecular interactions apparently rule out in this instance intermolecular interactions, responsible for the formation of associated forms $(RLi)_n$, typical for lithium alkyls and lithium alkenyls. The same factor can also account for the much lower values of K_d (approximately by two orders of magnitude) compared with the analogous values for hydrocarbon chains M_nMt.[5]

Results similar to those described above have been obtained for MAN.[111] The use of oligostyryl-lithium as the initial organometallic compound made it possible to obtain soluble blocks of "living" oligomers containing up to six MAN units in the chain. The dependence of the spectroscopic characteristics of these substances on the number of MAN units is illustrated in Fig. 5.

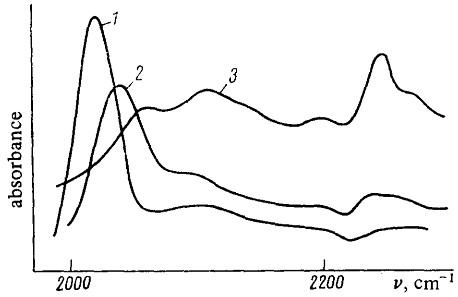
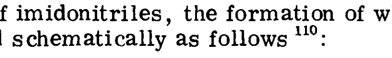


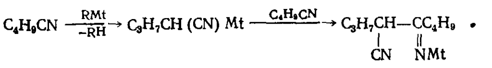
Figure 5. Infrared spectra of oligostyryl chains with terminal MAN units and a lithium counterion in benzene at 20° C.[110] Initial MAN :OStL molar ratio: 1) 1; 2) 2.2; 3) 5.5.

In order to achieve a correct assignment of the absorption bands and bands located in the intermediate region (between −2100 and 2200 cm^{-1}), the infrared spectra of model compounds based on valeronitrile (VN) and trimethylacetonitrile (TN) were obtained[110,111]. Oligostyryl-lithium was used as the organometallic component in these systems. When the ratio BH :RMt = 1 (with THF as the solvent), the infrared spectrum shows bands at 2030 (the most intense) and 2100 cm^{-1}. An increase of the BH :RMt ratio to three causes the disappearance of the first band and a significant increase of the intensity of the second. Treatment with ethanol of the reaction mixture obtained for the ratio BH :RMt = 3 causes the appearance of the spectroscopic characteristics of the equilibrium system[112]:



$$\underset{CN}{-CH}-\underset{NH}{C}- \rightleftarrows \underset{CN}{-C}=\underset{NH_2}{C}- .$$

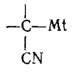
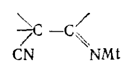
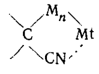
This is a direct indication of the presence in the initial reaction mixture of imidonitriles, the formation of which has been described schematically as follows[110]:



$$C_4H_9CN \xrightarrow[-RH]{RMt} C_3H_7CH(CN)Mt \xrightarrow{C_4H_9CN} C_3H_7\underset{CN}{\underset{|}{CH}}-\underset{NMt}{\underset{\|}{C}}C_4H_9 . \qquad (6)$$

Among the data obtained for systems with participation of TN, these for the interaction of TN with an active reagent containing a terminal MAN unit are of interest. Steric hindrance rules out in this instance the occurrence of a type (6) reaction and limits the interaction to complex formation, as shown by the appearance of a new band in the high-frequency region (2260 cm^{-1}), the intensity of which increases with increase of the concentration of any component. We may note that a small shoulder has been noted in this region in the infrared spectrum of chains with an increased number of MAN units (Fig. 5), which may be attributed to the formation of intramolecular complexes of the counterion with a nitrile group in the polymer chain.

The results described make it possible to adopt the following assignment of the infrared bands for the "living" AN and MAN chains:

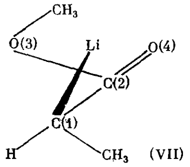
ν, cm^{-1}	2030—2050*	2100—2170	2250—2260
Group			
	(IV)	(V)	(VI)

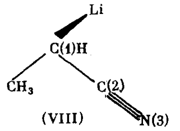
In real AN anionic polymerisation processes the formation of macromolecules is ensured by substances (IV). The formation of intra- or inter-molecular complexes of type (VI), which are capable of being converted into imidonitriles (V), is favoured when the reaction is carried out in non-polar media. The sequence of steps (IV) → (VI) → (V) is responsible for the low effectiveness of initiation in AN–RMt–hydrocarbon solvent systems; the formation of imides (V) is virtually equivalent to kinetic chain termination. The occurrence of the last reaction can be readily detected from the presence of carbonyl groups in deactivated AN polymers and oligomers[114,115].

The infrared spectra of compounds simulating the anionic active centres of methyl methylacrylate (MMA) are more difficult to interpret. Lochmann and Lim[116], who synthesised the compound $(CH_3)_2C(COOCH_3)Li$, attributed the absorption of its THF solution in the region of 1676 cm^{-1} to the carbonyl group; in the spectrum of the initial methyl isobutyrate the absorption at 1730 cm^{-1} corresponds to this group. According to Panayotov and coworkers[117,118], the absorption in the range 1605–1635 cm^{-1} (in THF) is characteristic of terminal MMA–Mt units, where Mt = Li, Na, or K. Zgonnik et al.[119] obtained the infrared spectra of the products of the interaction of various compounds RLi with MMA in non-polar media. The following absorption regions, referring to terminal units, were observed: 1620–1645, 1670–1680, and 1710–1755 cm^{-1}. The last of these may be due to the formation of intra- and inter-molecular complexes analogous to those noted above for "living" AN chains [see structure (VI)].

According to Figueruelo[120], the values of K_d for "living" MMA chains with Li^+ and K^+ counterions are 0.44×10^{-9} and 0.21×10^{-9} respectively (THF, −78° C). Quantities of a similar order of magnitude have been obtained[121] for "living" chains of 2-vinylpyridine (VP): 0.83×10^{-9} (Na); 2.45×10^{-9} (K); 1.05×10^{-9} (Cs) (in THF at 23° C). The different types of dependence of K_d on the nature of the counterion for "living" chains based on AN, MMA, and VP are striking. It appears that this is caused by the difference between the relative energy contributions; due to the decomposition of the intramolecular complexes and the solvation of the counterion.

The conclusion that there are intense intramolecular interactions in organometallic compounds with polar substituents agrees well with the results of quantum-chemical calculations by the CNDO/2 method for structures simulating the anionic AN and methyl acrylate active centres, namely $CH_3CH(Li)CN$ and $CH_3CH(Li)COOCH_3$.[80] Their optimum geometry indicates a significant mutual approach of the counterion and the polar group of the active centre:





	structure (VII)				structure (VIII)		
X	C (1)	C (2)	O (3)	O (4)	C (1)	C (2)	N (3)
Li—X, Å	2.2	2.4	2.9	3.0	2.1	2.2	2.8

IV. CONCLUSION

In conclusion we shall attempt to estimate the importance of information of the above kind for the determination of the mechanism of the formation of macromolecules in anionic systems. A detailed examination of this problem, different aspects of which have been discussed in many original and review publications (see, for example, Refs. 5, 62, 101, 122–125), is outside the framework of the main topic of the present review. We shall therefore confine ourselves to several comments on polymerisation under the influence of lithium compounds.

In all the "living" dienyl chains investigated the existence of only the 1,4 (or 4,1)-structure of the terminal unit has been noted with the predominant content of the *trans*-form in non-polar media and of the *cis*-form in ethereal media. When an attempt is made to reconcile this finding with the opposite type of structure of the polymers formed in the corresponding systems (the maximum content of the *cis*-1,4-units in polybutadiene and polyisoprene is reached in polymerisation in a non-polar medium), it is necessary to take into account at least two factors. The first and possibly the most important factor is that the fixation of the structure of the elementary unit of the growing chain occurs only after the addition of the succeeding monomer molecule to the terminal unit. This result indicates a conformational rearrangement of the terminal unit (characterised by a partly delocalised electronic structure) in the propagation stage. The second factor is the different states of organolithium compounds: stable associated species $(RM_nLi)_x$ in non-polar media and monomeric forms of the complexes $RM_nLi.mED$ in media of the ethereal type. At the same time, under the polymerisation conditions usually employed, the main contribution to the propagation reaction comes from the unassociated forms of the growing chains regardless of the nature of the medium. The experimental difference between the structures of the terminal units in media of different polarities cannot therefore be regarded as a basis for inferring the structural characteristics of the active centres operating in the same media. It is quite likely that the terminal units of the monomeric forms of the "living" polydiene chains with a lithium counterion have the *cis*-structure in non-polar media; this view can be found in the literature[56,126]. Another important problem concerns the 1,2-units (or 3,4-units) in polydienes, i.e. structural units whose appearance in macromolecules is most difficult to attribute to the direct experimental characteristics of the

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*Similar frequencies (2050–2071 cm^{-1}) were obtained by Yuchnovski[113] for lithioacetonitrile in polar solvents and in the solid state; the bands in this region were assigned to the ionic structure $(CH_2{=}C{=}N)^-Li^+$.

"living" chains. In relation to non-polar media, the solution of this problem may be based on the concentration (with respect to the growing chains) variation of the polymer structure; the content of vinyl(or isoprenyl) groups in polydienes increases with increase of the initiator concentration[56,91,127,128]. One of the possible explanations of this effect is the involvement of the associated forms of the growing chains in the progagation reaction and the increase of the relative contribution of these steps with increase of the initiator concentration[56,128]. According to Glaze et al.,[57] the reaction between the monomer and the associated species $(RM_nLi)_x$ can occur to a large extent as a result of attack on the γ-carbon atom of the terminal unit, since the α-carbon atom in the associated species is highly shielded. A natural consequence of the attack on the γ-carbon atom is the formation of 1,2- or 3,4-units. The decrease of the content of 1,4-units in polydienes on passing from non-polar to polar media and in the presence of catalytic amounts of polydentate electron donors can be explained similarly. We have in mind the partial shielding of the α-carbon atom in the solvation shell of a polar solvent surrounding the counterion, in the first instance, and the analogous effect in the formation of complexes of the active centres with electron donors containing bulky substituents or having large intrinsic dimensions, in the second. Together with steric considerations, account must be taken of the charge redistribution in the carbanionic fragment of the terminal unit on complex formation, namely the increase of the negative charge of the γ-carbon atom, which follows from NMR data[6,36,60,62].

We may note finally that the formation of intermediate complexes of the counterion with the monomer may be important for the microstructure of the polymers. In particular, the conformation of the monomer molecule in such complexes may be regarded as one of the factors determining the site of the attack on the terminal unit in the propagation stage. Unfortunately, this problem, as well as certain others among those discussed above, have not so far been studied experimentally. The quantum-chemical research technique applied to systems approaching real systems to the maximum possible extent may prove fruitful. Naturally the extent of studies in this field is still insufficient for more definite comments on this topic. Nevertheless the likely usefulness of this approach, which follows partly from the data presented in the present review, is evident from our point of view. The problem is discussed in greater detail by Eizner and Erusalimskii[129].

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Organophosphorus Compounds in 1,3-Dipolar Cycloaddition

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The cycloaddition of 1,3-dipoles to organophosphorus compounds containing a multiple bond is surveyed together with the reactions of phosphinylated 1,3-dipoles with various dipolarophiles, yielding five-membered heterocycles containing a phosphorus atom in either the ring or a side-chain. The Review covers also the "mixed dimerisation" of 1,3-dipoles with $\alpha\beta$-unsaturated compounds of tervalent phosphorus acting as 1,3-dipolar systems. A list of 146 references is included.

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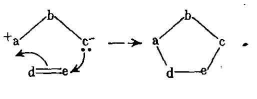
I. INTRODUCTION

1,3-Dipolar cycloaddition to unsaturated organophosphorus compounds forms an interesting and little studied branch of organophosphorus chemistry. The great structural variety both of 1,3-dipoles and of dipolarophiles makes this an important method for obtaining organophosphorus heterocycles that are difficult to prepare in other ways. Such addition can be defined as the interaction of a 1,3-dipole of general type $^{+}a-b-c^{-}$ with a multiple bond d=e accompanied by transfer of electrons within the cyclic transition state and by neutralisation of the formal charges[1]:



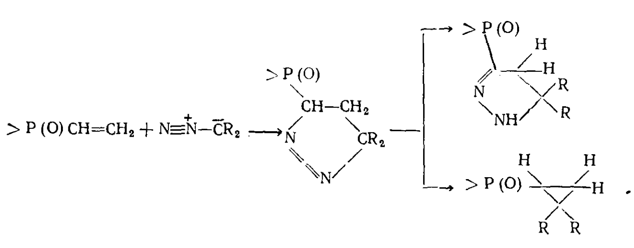
Despite the large number of investigations there is no generally accepted mechanism for 1,3-dipole cycloaddition. The majority of authors accept the single-stage mechanism first suggested by Huisgen[2,3], who regards such reactions as involving concerted but not necessarily simultaneous formation of two new σ bonds. This mechanism corresponds to a large negative entropy of activation and a moderate enthalpy of activation, a certain type of effect of substituents and solvent polarity, and *cis*-stereospecificity of addition[4,5]. Firestone[6-9] considers that a two-stage mechanism may also be possible, with intermediate formation of a diradical. A two-stage mechanism with an intermediate amphoteric compound has also been suggested[10]. In several papers the most important aspects of 1,3-dipolar cycloaddition, such as the effect of substituents, stereospecificity, regioselectivity, are discussed in terms of perturbation theory[11-14].

Considerable experimental information has now accumulated on 1,3-dipolar cycloaddition in the chemistry of organophosphorus compounds. The action of 1,3-dipoles on unsaturated compounds containing a four-coordinated phosphorus atom is a classical 3 + 2 → 5 cycloaddition. 1,3-Dipoles with phosphorus-containing substituents in a side-chain add to various dipolarophiles according to the same scheme. Reaction between $\alpha\beta$-unsaturated compounds containing tervalent phosphorus and 1,3-dipoles does not follow the usual scheme of 1,3-dipolar cycloaddition but a 3 + 3 → 6 scheme involving the phosphorus atom, with formation of six-membered heterocycles. This reaction can be regarded as mixed "dimerisation" of the 1,3-dipolar systems: under these conditions the phosphorus-containing component reacts similarly to other classical 1,3-dipoles. $\alpha\beta$-Unsaturated derivatives of three-coordinated phosphorus add to multiple bonds in various dipolarophiles according to a 3 + 2 → 5 scheme.

II. 1,3-DIPOLAR CYCLOADDITION TO ORGANOPHOSPHORUS COMPOUNDS CONTAINING MULTIPLE BONDS

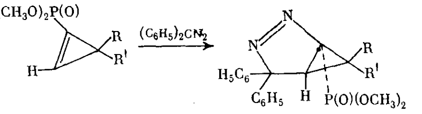
1. Phosphinylated Alkenes

Results on the addition of diazomethane to vinyl- and allyl-phosphonic esters were first published by Pudovik and his coworkers in 1964.[15] The cycloaddition of diazomethane[15-19], diphenyldiazomethane[20-25], phenyldiazomethane[26], diazopropane[26], diazoacetic ester[27,28], and 9-diazofluorene[29] to such phosphonic esters involves intermediate formation of Δ^1-pyrazolines, which either eliminate nitrogen and pass into cyclopropane derivatives or isomerise into thermodynamically stable Δ^2-pyrazolines depending on the experimental conditions:



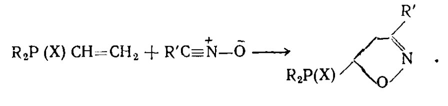
In contrast to other diazoalkanes, diazoacetic ester gives with vinylphosphonates mixtures of isomeric Δ^2-pyrazolines differing in the positions of the phosphinyl and alkoxycarbonyl groups in the ring[27]. At higher temperatures the reactions of diazoalkanes with vinyl- and allylphosphonates yield cyclopropane derivatives.

The kinetics of the cycloaddition of diphenyldiazomethane to vinylphosphonates and vinylphosphine oxides is consistent with a single-stage multicentre process with cyclic electron transfer[25]. The cycloaddition of diphenyldiazomethane at the strained double bond in phosphinylcyclopropenes leads to the formation of substituted diazabicyclo[3,1,0]hexenes[30]:



(*a*) $R=R'=CH_3$; (*b*) $R=CH_3$, $R'=C_6H_5$.

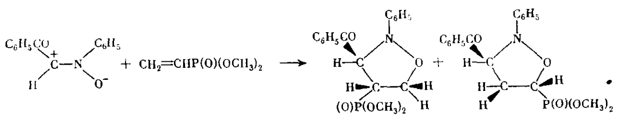
Nitrilimines, nitrile oxides, and nitrones also undergo 1,3-dipolar cycloaddition to vinylphosphonic esters and the tetramethyldiamide and to diphenylvinylphosphine oxide and sulphide[31]. Nitrilimines form 5-phosphinyl-Δ^2-pyrazolines, whereas the *N*-oxides of aceto- and benzonitrile yield 5-phosphinyl-2-isoxazolines:



The rate of addition of diphenylnitrilimine to unsaturated organophosphorus compounds increases with the electrophilicity of the ethylenic double bond. Comparison of the relative addition rate constants indicates that in the case of benzonitrile *N*-oxide the sequence of dipolarophilic activity of unsaturated organophosphorus compounds does not coincide with their activity sequence on reaction with diphenylnitrilimine. This is attributed to differences in the way in which σ bonds are formed in the transition state in these reactions[32].

In the cycloaddition of benzaldehyde *N*-phenyloxime to dimethyl vinylphosphonate the phosphinyl group occupies position 4 in the isoxazolidine ring according to Arbuzov et al.[33], in contrast to Kolokol'tseva et al.[31] Stereochemical investigation has established the *trans*-configuration for substituents in the isoxazolidine rings formed on the addition of this nitrone to vinylphosphonic and β-cyanovinylphosphonic esters, as well as to methyl β-diethoxyphosphinylacrylate[33,34].

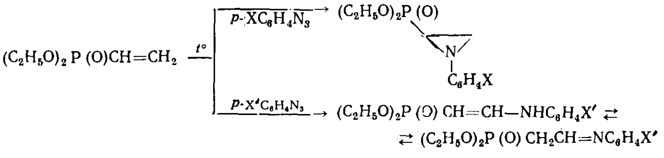
Phenylglyoxal *N*-phenylmonoxime adds to dimethyl vinylphosphonate at 20°C to form isomeric isoxazolidines corresponding to different orientations of dipole and dipolarophile[35]:



In boiling benzene only the first isomer is obtained. Cycloaddition of the nitrone to diethyl vinylphosphonate also yields only 4-diethoxyphosphinylisoxazolidine. Dimethyl allylphosphonate adds nitrones to form isoxazolodines containing a 5-phosphinyl group[35]. Potassium diethyl β-hydroxyvinylphosphonate reacts with toluene-*p*-sulphonyl azide to give a diazophosphonic ester and a potassium salt of formyltoluene-*p*-sulphonamide[36], with possible intermediate formation of a phosphorus-containing triazoline.

Aryl azides react with vinylphosphonates at room temperature[37,38] to form Δ^2-triazolines containing a phosphinyl group at position 4. To prove the orientation of addition of the azide use was made of the ability of the triazoline ring to cleave into a linear diazo-derivative in the presence of a base. Cycloaddition of *p*-nitrophenyl azide to a β-diethylaminovinylphosphonate yields a 4-phosphinyl-1,2,3-triazole as a consequence of elimination of diethylamine from the triazoline formed initially[38].

When heated (75–80°C) aryl azides react with β-cyanovinyl-, propenyl-, and vinyl-phosphonates to form aziridines[37–39]. It is interesting that, when the azide contains donor substituents, cycloaddition leads only to phosphinylaziridines, but in the presence of acceptor substituents an enamine is also formed:



$X = CH_3O$, CH_3, H, Br; $X' = Br$, NO_2.

Differential thermal analysis with quantitative measurement of gas evolution has shown that thermal reactions between phenyl azide and vinylphosphonates involve intermediate formation of Δ^2-triazolines, which under the experimental conditions break down with evolution of nitrogen and formation of aziridines.

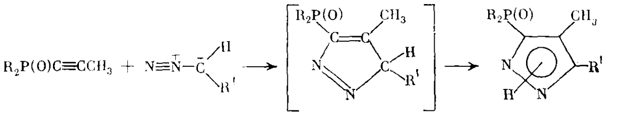
Table 1. Rate constants (10^3k_2, M^{-1} min^{-1}) for the reactions of azides *p*-$XC_6H_4N_3$ with vinylphosphonates $(C_2H_5O)_2.PO.CH:CHY$ in xylene at 115°C.

X	$Y = PO(OC_2H_5)_2$	Y=H			$Y=N(C_2H_5)_2$
	10^3k_2	10^3k_2	$E^{\neq}$, kcal $mole^{-1}$	$\Delta S^{\neq}$, e.u.	10^3k_2
NO_2	5.60	16.5	18.0	−31.1	55.5
Br	6.80	13.7	—	—	6,08
H	6.55	12.6	17.2	−33.5	1.40
CH_3	7.65	12.1	—	—	0,93
CH_3O	8.70	18.0	15.7	−36,3	0.89

Kinetic investigation of the cycloaddition of aryl azides to phosphinylated ethylenes[38] has shown (Table 1) that the reactions of a diphosphinylethylene with azides are of the "dipolarophile–acceptor, 1,3-dipole–donor" type (reactions controlled by highest occupied orbital[13,14]), whereas the reactions of azides with a β-diethylaminovinylphosphonate are of the "dipolarophile–donor, 1,3-dipole-acceptor" type. Both donor and acceptor substituents accelerate the reaction of phenyl azides with diethyl vinylphosphonate. Donor–acceptor interaction of "neutral" type probably operates in this case (reactions controlled by highest occupied and lowest unoccupied orbitals). Reactivity of the aryl azide–vinylphosphonate system is determined mainly by intermolecular donor–acceptor interactions, which stabilise the transition state and depend on the donor–acceptor properties of the reactants.

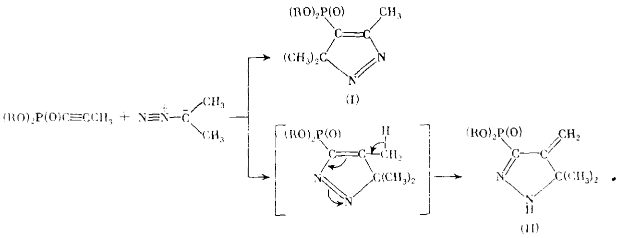
2. Phosphinylated Alkynes

In 1963 Saunders and Simpson obtained an *N*-methylated phosphinylpyrazole by the action of diazomethane on di-isopropyl ethynylphosphonate[40]. A little later the cycloaddition of diazomethane to a diphosphinylacetylene to form a diphosphinylpyrazole was accomplished[41]. With propynylphosphonates and propynylphosphine oxides diazoalkanes also form the corresponding 3(5)-phosphinylated pyrazoles[42,43]:



R = AlkO, Alk, Ar; R' = H, $CO_2C_2H_5$.

Formation of an intermediate phosphinylpyrazolenine in the 1,3-dipolar cycloaddition of diazoalkanes to phosphinylacetylenes is confirmed in the reactions of disubstituted diazo-compounds with a triple bond. The cycloaddition of 2-diazopropane to propynylphosphonates[44] yields a mixture of a 4-dialkoxyphosphinyl-3,5,5-trimethylpyrazolenine (I) and a 3-dialkoxyphosphinyl-5,5-dimethyl-4-methylene-Δ^2-pyrazoline (II) (in the proportions 60 : 40):



The first stage produces a mixture of pyrazolenines differing in the position of the phosphinyl group in the ring. The 3-dialkoxyphosphinylpyrazolenine undergoes prototropic isomerisation into the phosphinyl-Δ^2-pyrazoline. Prototropic isomerisation of a 4-phosphinylpyrazolenine is impossible.

Study of the cycloaddition of diazoacetic ester to propynylphosphonates and propynylphosphine oxides by differential thermal analysis enables[43] F-substituents to be ranged in the sequence

$$C_6H_5 \simeq C_2H_5 > C_2H_5O \sim C_3H_7O \sim C_4H_9O > Cl$$

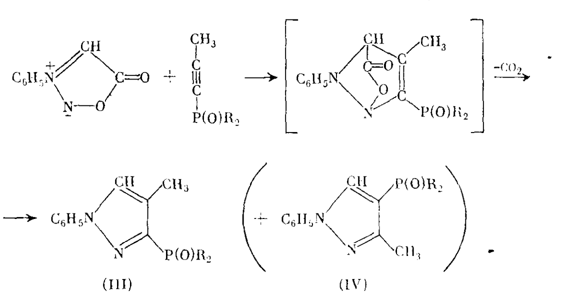
according to their effect in raising the temperature at which the exothermic effect begins. The dipolarophilic activity of the triple bond in the above compounds obviously increases in the same sequence, owing to the diminution in the electron-accepting properties of the phosphinyl group.

Table 2. Rate constants (10^3k_2, M^{-1} min^{-1} for the cycloaddition of azides p-$XC_6H_4N_3$ to diethyl ethynylphosphonates $(C_2H_5O)_2PO.C\vdots CY$ in m-xylene at 115°C.

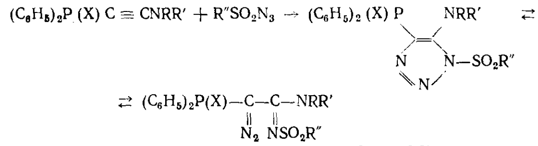
Y	X=NO_2	X-Br	X=H			X=CH_3	X=OCH_3
	10^3k_2	10^3k_2	10^3k_2	$E^{\neq}$, kcal mole^{-1}	$\Delta S^{\neq}$, e.u.	10^3k_2	10^3k_2
$(C_2H_5O)_2P(O)$	22.1	32.1	33.1	16.6	—32.9	36.2	43.2
Cl	4.40	6.28	7.50	17.9	—32.7	8.53	9.82
CH_3	3.47	2.20	3.10	18.7	—32.5	3.80	4.66
$N(C_2H_5)_2$	2.11	44.0	15.4	16.8	—34.2	11.6	8 56

Pyrazoles containing a phosphinyl group at the 3-position are formed by the addition of diazomethane to ethynyldiphenylphosphine and its oxide[45]. Methyl β-diphenylphosphinopropiolate forms with diazomethane a mixture of two isomeric pyrazoles corresponding to different orientations of the dipole relative to the dipolarophile[45].

The cycloaddition of N-phenylsydnone to propynylphosphonates, propynylphosphonothioates, and propynyldiphenylphosphine oxide[46] involves fixation of a dipole nitrogen atom mainly on the dipolarophile α-carbon atom [proportions of isomers (III) : (IV) = 85 : 15]:



The addition of organic azides to phosphinylethynylamines yields triazoles contaminated with diazo-compounds[47], the quantity of which depends on the nature of the substituents:

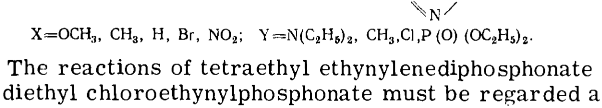


X=O, S, Se, NSO_2R''; R=CH_3, C_2H_5, C_6H_5, p-$CH_3C_6H_4$; R'=C_2H_5, C_6H_5; R''=C_6H_5, p-$CH_3C_6H_4$, $(CH_3)_3C_6H_2$, p-$NO_2C_6H_4$.

Thus, when the substituents R and R' have a high $-M$ effect, the tautomeric triazole form is absent.

The cycloaddition of aryl azides to propynylphosphonates and propynylphosphine oxides is regioselective and leads to the formation of triazoles having the phosphinyl group in the 4-position[48-51]. The structure of the adducts has been established by infrared spectroscopy, ^1H and $^1H-\{^{31}P\}$ nuclear magnetic resonance spectroscopy, and the nuclear Overhauser effect.

The reactivity of phosphinylacetylenes towards azides is increased both by donor and by acceptor substituents Y in the β position of the dipolarophile[52,53] (Table 2):



X=OCH_3, CH_3, H, Br, NO_2; Y=$N(C_2H_5)_2$, CH_3,Cl,P(O)$(OC_2H_5)_2$.

The reactions of tetraethyl ethynylenediphosphonate and of diethyl chloroethynylphosphonate must be regarded as belonging to the "dipolarophile–acceptor, 1,3-dipole–donor" type, in which interaction between the highest occupied orbital of the dipole and the lowest unoccupied orbital of the dipolarophile predominates. Those of diethyl diethylaminoethynylphosphonate with azides are of the "dipole–acceptor, dipolarophile–donor" type. Kinetic study of the reactions of diethyl propynylphosphonate with aryl azides has shown that neither electron-donor nor electron-acceptor substituents in the azide accelerate the reaction significantly.

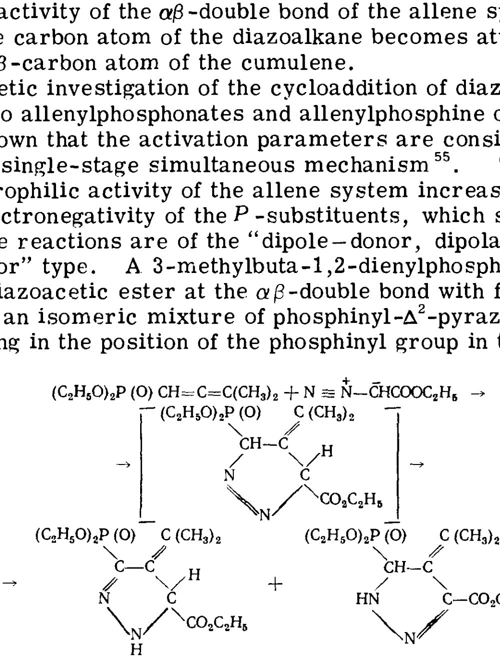
In a series of $para$-substituted phenyl azides the sensitivity of the reactivity to the activating influence of donor substituents in the phosphinylacetylenes diminishes and the sensitivity to acceptor substituents increases. This involves inversion from the "dipole–acceptor, dipolarophile–donor" type of reaction through the region of "neutral" cycloaddition to the "dipole–donor, dipolarophile–acceptor" type. Comparison of the logarithms of the rate constants for propynylphosphine oxides (measured at 115°C) with the Kabachnik σ^f constants has shown that the dipolarophilic activity of the triple bond intensifies as substituents attached to the phosphorus atom ($\rho = 0.24$, $r = 0.993$) become more electronegative. Propynylphosphonates do not conform to this correlation. The factors governing the reactivity of these dipolarophiles towards azides are evidently not described by specific phosphorus constants. The variation in the relative reactivity of these systems may be significantly influenced not only by changes in the donor–acceptor properties of the ligands but also by changes in their localisation energies.

These results taken together suggest that the reactivity of 1,3-dipoles and dipolarophiles is a consequence mainly of the highest occupied orbital–lowest unoccupied orbital model, and is consistent with a concerted reaction mechanism. The large negative entropies of activation, indicating a high degree of order in the transition state, and the moderate energies of activation agree with a single-stage multicentre mechanism. The observed slight dependence of rate of addition on solvent polarity is inconsistent with a two-stage mechanism involving an intermediate zwitterion. The weak sensitivity of the reactivity to interchange of substituents in the ligands is also evidence of the insignificant polarity of the transition state.

3. Phosphinylated Allenes

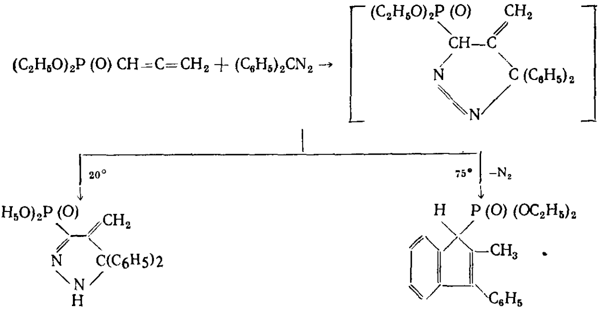
The cycloaddition of unsubstituted and monosubstituted diazoalkanes to phosphinylalenes yields phosphinylated pyrazoles[42]. The activating influence of the electron-accepting phosphinyl group is responsible for the dipolarophilic activity of the $\alpha\beta$-double bond of the allene system, and the carbon atom of the diazoalkane becomes attached to the β-carbon atom of the cumulene.

Kinetic investigation of the cycloaddition of diazoacetic ester to allenylphosphonates and allenylphosphine oxides has shown that the activation parameters are consistent with a single-stage simultaneous mechanism[55]. The dipolarophilic activity of the allene system increases with the electronegativity of the P-substituents, which suggests that the reactions are of the "dipole–donor, dipolarophile–acceptor" type. A 3-methylbuta-1,2-dienylphosphonate adds diazoacetic ester at the $\alpha\beta$-double bond with formation of an isomeric mixture of phosphinyl-Δ^2-pyrazolines differing in the position of the phosphinyl group in the ring[43]:



$(C_2H_5O)_2P(O)CH{=}C{=}C(CH_3)_2 + \overset{+}{N}{\equiv}N{-}\overset{-}{C}HCOOC_2H_5 \rightarrow$

Depending on the temperature the thermodynamically unstable Δ^1-pyrazoline formed on the cycloaddition of diphenyldiazomethane to diethyl allenylphosphonate[54] may either isomerise into the Δ^2-pyrazoline or decompose with the evolution of nitrogen and the formation of a phosphinylated indene:

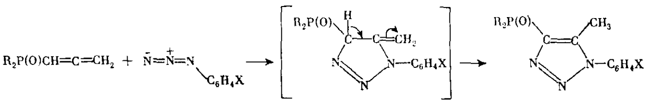


A 1-phenylpropa-1,2-dienylphosphonate with diphenyldiazomethane forms a methylenecyclopropane derivative. 2-Diazopropane reacts with allenylphosphonates at room temperature to give dialkyl 5,5-dimethyl-4-methylene-Δ^2-pyrazol-3-ylphosphonates[44]. The cycloaddition of N-phenylsydnone to allenylphosphonates and allenylphosphine oxides[56,57] produces a mixture of isomeric pyrazoles having different orientations of the dipole with respect to the dipolarophile.

Table 3. Rate constants (10^3k_2, $M^{-1}\ min^{-1}$) for the reactions of aryl azides p-$XC_6H_4N_3$ with phosphinylated allenes $R_2PO.CH:C:CH_2$.

R	X				
	NO_2	Br	H	CH_3	CH_3O
Cl	1.25	5.88	9.30	15.1	19.9
C_2H_5O	1.30	1.15	1.04	1.50	1.99
$N(CH_3)_2$	113.4	16.0	6.03	4.00	3.30

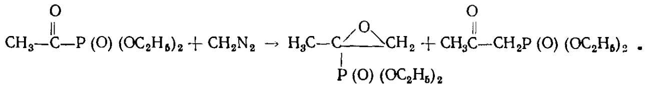
The Δ^1-triazolines having an exocyclic methylene group that are formed by the cycloaddition of aryl azides to phosphinylated cumulenes are very unstable, and are stabilised by prototropic isomerisation into triazoles[38]:



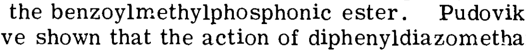
A kinetic study has been made[38] of the reactions of *para*-substituted aryl azides with phosphinylated allenes containing electron-accepting (chloro) and weakly and strongly electron-donor (ethoxy and dimethylamino) substituents attached to the phosphorus atom[38]. The reaction of allenylphosphonic dichloride is accelerated by donor and retarded by acceptor substituents in the aryl azide. Comparison of the logarithms of the reaction rate constants (Table 3) with the Hammett σ constants reveals a good linear dependence ($\rho = -0.85$, $r = 0.996$); the reaction belongs to the "dipolarophile–acceptor, 1,3-dipole–donor" type. The action of aryl azides on allenylphosphonic bisdimethylamide must be regarded as the "dipolarophile–donor, dipole–acceptor" type. Donor–acceptor interaction of "neutral" type occurs in the reactions of diethyl allenylphosphonate with aryl azides, as in those of diethyl propynylphosphonate and vinylphosphonate. The reactivity of the ligands is obviously determined by the electronic effects of the *P*-substituents, and the phosphorus atom iself participates in transmitting the effects of the substituents to the reactive centre[38].

4. α-Oxo-phosphonates

In 1963 Arbuzov et al.[58] studied the reaction of diazomethane with diethyl acetylphosphonate, from which diethyl 2-methyloxiran-2-ylphosphonate and a small quantity of diethyl acetonylphosphonate were obtained:



The action of diazomethane on diethyl benzoylphosphonate gives only the benzoylmethylphosphonic ester. Pudovik et al.[59] have shown that the action of diphenyldiazomethane on derivatives of acetyl- and benzoyl-phosphonic acids at high temperatures yields products of oxiran structure. The latter was confirmed by infrared spectral data and by the catalytic and thermal isomerisation of the products with rupture of a cyclic carbon–oxygen bond and formation of a phosphinyl ketone. More recently β-keto-phosphonates have been obtained[60] by the action of diazomethane and phenyldiazomethane on benzoylphosphonates under similar conditions:

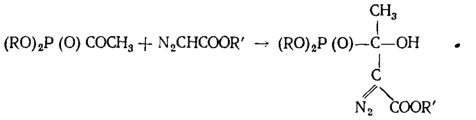


$$\underset{\underset{O}{\|}}{R-C}-P(O)(OR')_2 + R''CHN_2 \rightarrow \underset{\underset{O}{\|}}{R-C}-CHR''P(O)(OR')_2$$

$R=C_6H_5$, m-ClC_6H_4, p-$CH_3OC_6H_4$; $R'=C_2H_5$, CH_3; $R''=H$, C_6H_5.

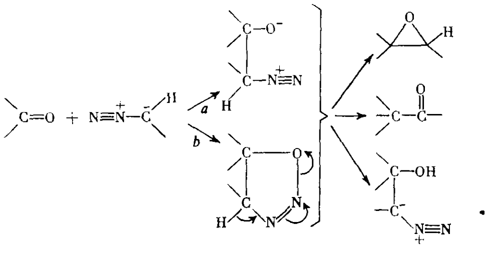
It is assumed[60] that such reactions involve migration of the phosphinyl group to form the thermodynamically stable β-keto-phosphonates. The action of diazoethane on α-oxo-phosphinyl compounds yields exclusively the corresponding β-keto-phosphinyl derivatives[61,62].

Diazoacetic esters form adducts of "aldol" type—alkyl β-dialkoxyphosphinyl-α-diazo-β-hydroxybutyrates[63,64]:



$$(RO)_2P(O)COCH_3 + N_2CHCOOR' \rightarrow (RO)_2P(O)-\overset{\overset{CH_3}{|}}{\underset{\underset{\underset{N_2 \quad COOR'}{C}}{|}}{C}}-OH$$

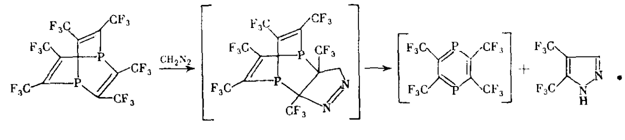
The mechanism of the reactions of diazoalkanes with α-oxo-phosphonates is represented by the general scheme[64]



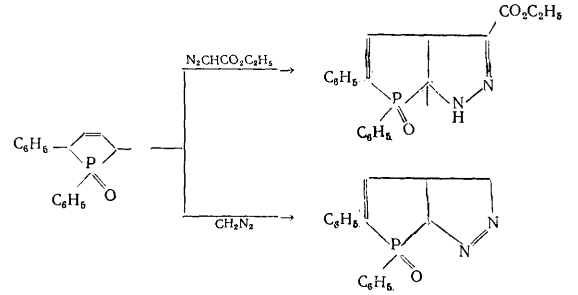
Reaction path (*a*) presupposes formation of a zwitterion in the first stage; path (*b*) involves 1,3-dipole cycloaddition, with formation of a 1,2,3-oxadiazoline derivative in the first stage. The products may be oxirans, β-keto-phosphonates, and diazohydroxyalkylphosphonates. The direction of the reaction of α-oxo-phosphonates with diazoalkanes is significantly influenced by the nature of the substituents both adjacent to the carbonyl group[58,59] and attached to the carbon atom of the diazo-component[59,61,63,64].

5. Tertiary Cyclic Phosphines and their Oxides

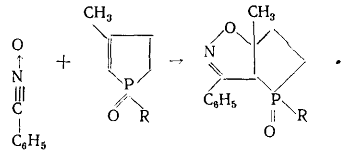
A substituted diphosphabarrelene behaves as a dipolarophile, undergoing addition at the multiple bond in diazomethane and phenyl azide[65]. However, the adducts formed by cycloaddition are unstable:



The 1,3-dipolar cycloaddition of diazoalkanes to 1,2,5-triphenylphosphole oxide yields adducts of dihydropyrazole structure[66,67]:



Δ^2-Phospholens form with oxides of aromatic nitriles derivatives of oxazaphosphabicyclo[3,3,0]octene[68]:

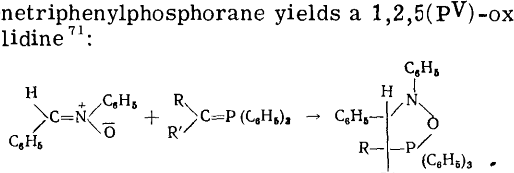


In the case of Δ^3-phospholen the sequence in which the nitrile oxide is added has no significance, because of the symmetry of the former molecule.

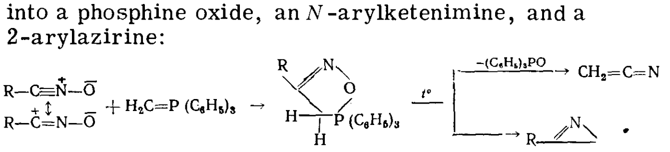
6. Alkylidenephosphoranes

The cycloaddition of 1,3-dipoles to alkylidenephosphoranes produces five-membered heterocycles containing the phosphorus atom either directly in the ring or in a side-chain. Methylene- and imino-phosphoranes have been subjected to reaction with nitrones[69–71], nitrile oxides[70,72–75], nitrilimines, and other 1,3-dipoles[70,76].

Reaction between benzaldehyde *N*-phenyloxime and an alkylidenetriphenylphosphorane yields a 1,2,5(P^V)-oxazaphospholidine[71]:



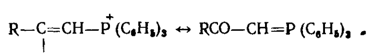
Benzonitrile oxide adds to methylenetriphenylphosphorane to form an oxazaphospholen, which breaks down at 140°C into a phosphine oxide, an *N*-arylketenimine, and a 2-arylazirine:



Huisgen and Wulff suggest[75] a multicentre single-stage addition for these reactions. The direction of cycloaddition is determined by the principle of maximum gain in energy of the σ bond, with consequent formation of an energetically favourable phosphorus–oxygen bond.

Iminophosphoranes are less active as dipolarophiles than are methylenephosphoranes. Cycloadducts of the latter with a nitrile oxide and a nitrone are quite stable and can be isolated, but with iminophosphoranes only decomposition products of the initial adducts are obtained. Thus the adduct of phenylglyoxal *N*-phenylmonoxime and phenyliminotriethylphosphorane eliminates a phosphine oxide to form N^2-benzoyl-N^1N^1-diphenylformamidine[70].

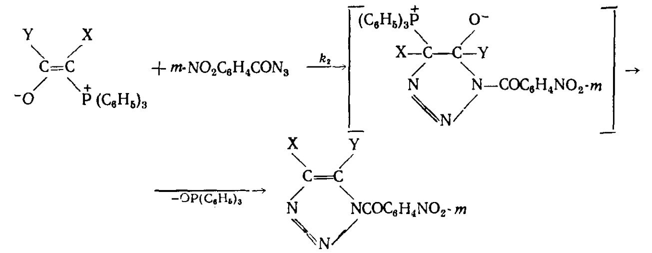
In contrast to methylene- and imino-phosphoranes, β-oxoalkylidenephosphoranes are able to react with 1,3-dipoles in the form of two resonance structures[77]



$$\underset{-O}{R-C}=CH-\overset{+}{P}(C_6H_5)_3 \leftrightarrow RCO-CH=P(C_6H_5)_3\,.$$

1,3-Dipolar cycloaddition of organic azides[77–81] to β-oxoalkylidenephosphoranes gives a mixture of products formed by incorporation into the phosphorane (*a*) at the C=C bond (triazoles and phosphine oxides) and (*b*) at the C=P bond (phosphoranes), one of which may predominate depending on the substituent in the initial phosphorane or on the conditions[77,82–84]. Benzonitrile oxides resemble azides in reacting with acylmethylenetriphenylphosphoranes to give a mixture of an isoxazole and a new phosphorane[82].

The mechanism of the reaction of azides with β-oxoalkylidenephosphoranes has been clarified by means of the kinetic investigations[77,80]

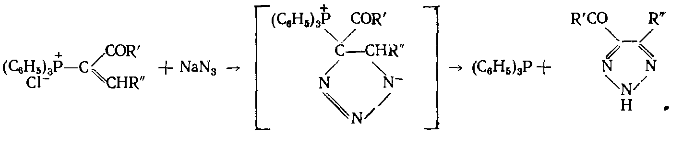


$Y=CH_3$, C_6H_5, $p\text{-}NO_2C_6H_4$.

The activation parameters are consistent with 1,3-dipolar cycloaddition. It is considered[80] that concerted formation of σ bonds takes place, but at different rates.

7. Vinylphosphonium Salts

Cycloaddition of inorganic azides[85,86] or diazoalkanes[87–90] to vinylphosphonium salts takes place at the double bond by a 3 + 2 → 5 scheme with the formation of heterocycles containing the phosphorus atom in a side-chain. Cycloaddition of sodium azide to a vinylphosphonium salt produces an unstable adduct, which splits into triphenylphosphine and a triazole:



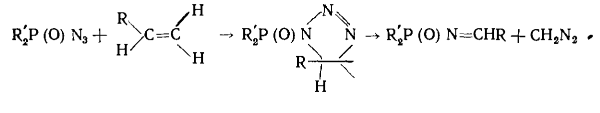
Stable 2-pyrazol-3-yltriphenylphosphonium bromides have been obtained[88] by the cycloaddition of diazoalkanes to unsubstituted vinylphosphonium salts. The action of diazo-compounds on β-acylvinylphosphonium salts gives pyrazoles and a phosphine oxide[89]. The direction of cycloaddition is controlled by the electronic and steric effects of the substituents and also by the reaction conditions.

III. 1,3-DIPOLAR CYCLOADDITION OF PHOSPHINYLATED 1,3-DIPOLES

1. 1,3-Dipoles containing Phosphinyl Substituents in a Side-chain

The cycloaddition of diazoalkanephosphonates to various unsaturated compounds yields phosphinylated pyrazoles and pyrazolines[91–104]. The dependence of the vicinal spin–spin coupling constant of phosphorus-31 and hydrogen-1 nuclei on the dihedral angle found from the nuclear magnetic resonance spectra has been used to determine the configurations of the Δ^1-pyrazolines formed by the cycloaddition of a diazoalkanephosphonate to norbornene and norbornadiene[102]. Electronic factors play an important part in the formation of configurational isomers epimeric with respect to the 3-carbon atom in the pyrazoline. The conformation has been determined for the Δ^1-pyrazolines obtained by 1,3-dipolar cycloaddition of ethyl α-diazo-β-dimethoxyphosphinyl-β-hydroxybutyrate to methyl methacrylate[104]. Reaction of this butyrate with dimethyl acetylenedicarboxylate is accompanied by decomposition of the resulting diastereomeric pyrazolenines as a consequence of rupture of phosphorus–carbon and carbon–carbon bonds[105].

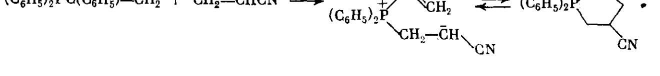
Phosphinyl azides add at multiple bonds in unsaturated compounds:



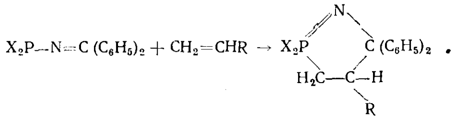
The reaction products are in one case stable triazolines[106–108], and in another *N*-phosphinylated imines and diazomethane both formed on decomposition of unstable initial adducts[109]. Diphenyl phosphorazidate reacts with enamines of cyclic ketones to form unstable triazolines, which evolve nitrogen and give products of ring contradiction[110].

2. αβ-Unsaturated Phosphines and Phosphinites

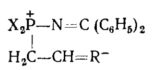
αβ-Unsaturated compounds containing a three-coordinated phosphorus atom react with such dipolarophiles as acrylates, acetylenedicarboxylic esters, and derivatives of α-keto-carboxylic acids by adding to C=C, C≡C, and C=O multiple bonds according to the classic 3 + 2 → 5 scheme. Thus 1,3-dipolar cycloaddition of diphenyl-1-phenylvinylphosphine (dipole of type $=\ddot{P}-C=C$) to acrylonitrile yields a cyclic adduct[111]:



A substituted methyleneaminophosphine adds to acrylonitrile or methyl acrylate to form a Δ^1-1,2-aza-(PV)-phospholine, the first cyclic phosphazen containing fewer than six atoms in the ring[112,113]:

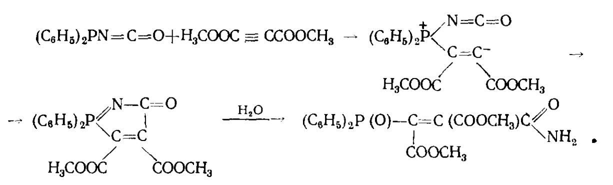


A betaine structure



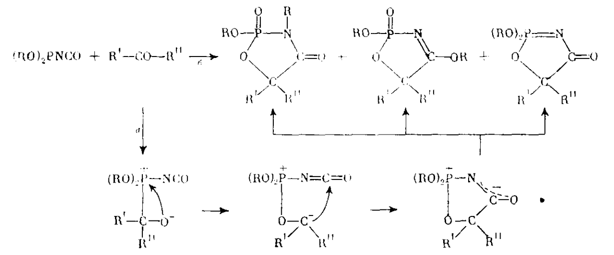
may well be formed as an intermediate stage[112,113]. Cycloaddition of diethoxymethyleneaminophosphines to acrylic esters gives derivatives of dihydroazaphospholopyridine[114].

The reaction of isocyanatodiphenylphosphine with dimethyl acetylenedicarboxylate is regarded[115] as involving an intermediate zwitterion, which cyclises into an unstable five-membered heterocycle readily hydrolysed to a phosphine oxide:

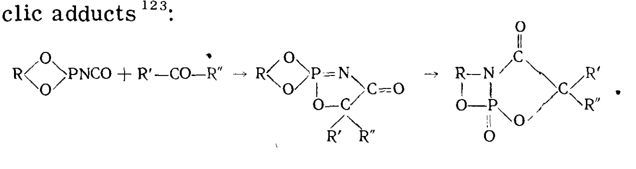


Diethyl phosphoramidinate reacts readily with acetylenedicarboxylic and maleic esters[116] to form azaphospholes and azaphospholines.

The carbonyl group also exhibits dipolarophilic activity towards phosphorisocyanatidites and methyleneaminophosphines. These esters react with esters[117,118,125,126,128] and nitriles[119,128] of α-oxo-carboxylic acids, with α-dicarbonyl compounds[120,121], and with α-oxo-phosphonates[126,127], forming mixtures of structurally isomeric substituted oxazaphospholidinones, oxazaphospholines, and oxazaphospholinones. Reaction is assumed[128] to follow path (a):

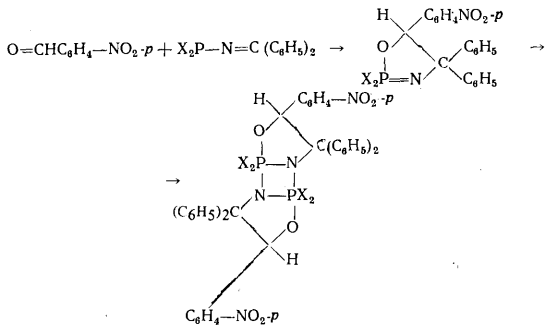


The reactions of isocyanatodiphenylphosphine and of phosphorisocyanatidous tetraethyldiamide with ethyl pyruvate go in the same direction, forming substituted oxazaphospholines, which contain a phosphimide bond[122]. Alkylene glycol esters of isocyanates of phosphorous acid form with α-oxo-carboxylic esters and phenylglyoxal 1 : 1 bicyclic adducts[123]:



Substituted bicycloheptanes are obtained by the action of carbonyl compounds on ethyl phosphorodi-isocyanatidite[124].

Cycloaddition of a substituted methyleneaminophosphine to p-nitrobenzaldehyde gives a dimeric 1 : 1 adduct[129]:



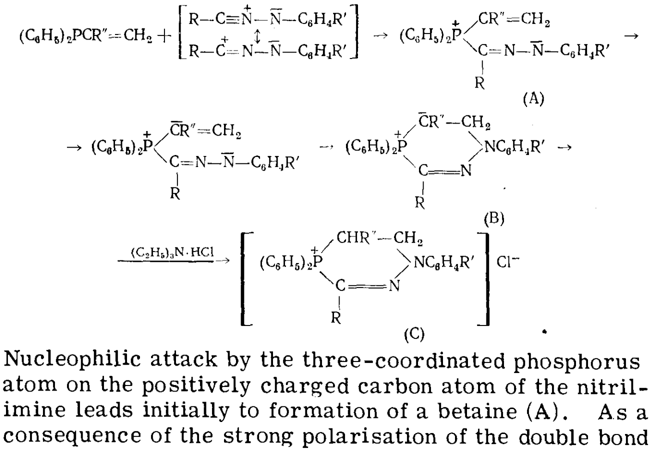
The ability of $\alpha\beta$-unsaturated compounds containing tervalent phosphorus to react as 1,3-dipolar systems is attributed[130,131] to the behaviour of the phosphorus atom as a nucleophile in virtue of its lone pair of electrons. On becoming quaternised, the phosphorus atom develops π-acceptor properties as a consequence of $d\pi - p\pi$ conjugation, activating the β position of the multiple bond. It is considered[130,131] that any system of the type $\ddot{Z}-X=Y$ can react as a 1,3-dipole, where $\ddot{Z}$ is an element having a lone pair of electrons, while X and Y are elements capable of forming π bonds.

IV. MIXED "DIMERISATION" of 1,3-DIPOLES AND $\alpha\beta$-UNSATURATED PHOSPHINES AND PHOSPHONITES

1. Ethylenic and Acetylenic Phosphines and Phosphonites

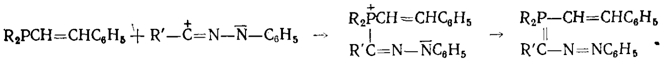
As well as reactions in which $\alpha\beta$-unsaturated compounds containing three-coordinated phosphorus behave as 1,3-dipolar systems, these substances also undergo mixed "dimerisation" with classic 1,3-dipoles.

Vinyl-, isopropenyl-, allyl, and alkynyl-phosphines react with substituted nitrilimines according to a 3 + 3 → 6 scheme involving the phosphorus atom to form (in the presence of triethylamine hydrochloride) six-membered cyclic phosphonium salts[132-134,137,138,146]:



Nucleophilic attack by the three-coordinated phosphorus atom on the positively charged carbon atom of the nitrilimine leads initially to formation of a betaine (A). As a consequence of the strong polarisation of the double bond due to the positively charged phosphorus atom, the betaine cyclises into a phosphorine (B), which is then converted into a phosphonium salt (C). The reaction of $\alpha\beta$-unsaturated ethylenic and acetylenic phosphonites with nitrilimines proceeds similarly, but the concluding stage is accompanied by an Arbuzov rearrangement[135,136,139,140].

Alkynylphosphonous tetra-alkyldiamides react with diphenylnitrilimine to form cyclic phosphonium salts, derivatives of 1,4-dihydro-4-phosphapyridazine[141]. Reaction between nitrilimines having electron-accepting groups attached to the carbon atom and β-substituted ethylenic and acetylenic dialkyl-, diamino-, and diphenylphosphines gives azomethylenephosphoranes[134,141]:



$$R_2PCH{=}CHC_6H_5 + R'{-}\overset{+}{C}{=}N{-}\overline{N}{-}C_6H_5 \rightarrow \begin{matrix} R_2\overset{+}{P}CH{=}CHC_6H_5 \\ | \\ R'C{=}N{-}\overline{N}C_6H_5 \end{matrix} \rightarrow \begin{matrix} R_2P{-}CH{=}CHC_6H_5 \\ \| \\ R'C{-}N{=}NC_6H_5 \end{matrix} .$$

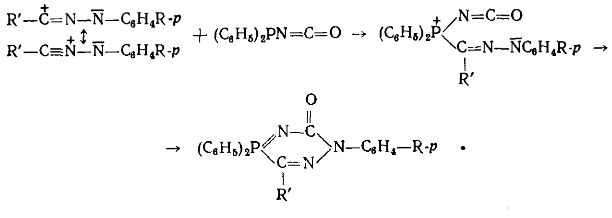
The nature (saturated or aromatic) of substituents attached to the phosphorus atom has no effect on the course of the reaction. With αβ-ethylenic phosphines and phosphonites this is determined mainly by two factors—steric hindrance by β-substituents in the unsaturated group and the nature of the substituents attached to the carbon atom of the nitrilimine. The reactions of acetylenic derivatives of tervalent phosphorus with nitrilimines, in contrast to those of ethylenic compounds, are less sensitive to steric hindrance at the β-carbon atom of the ethynyl group and to the nature of substituents attached to the nitrilimine carbon atom[137]. This difference in behaviour is attributed[137] to greater activity of the *sp*-hybridised carbon atom in reactions with nucleophilic reagents.

Kinetic investigation by the method of competing reactions has shown[141] that the reactivity of unsaturated derivatives of three-coordinated phosphorus towards nitrilimines is determined primarily by the inductive effects of the substituents and to a less extent by the $d\pi - p\pi$ conjugation. Comparison of the relative rate constants for reactions of a series of αβ-unsaturated compounds of tervalent phosphorus with diphenylnitrilimine suggests[141] a two-stage nucleophilic mechanism. The rate-determining stage is nucleophilic attack by the phosphorus atom on the electron-deficient carbon atom of the nitrilimine. Thus the rules of mixed "dimerisation" differ from those of classic 1,3-dipolar cycloaddition.

Study of the reactions of organic azides with αβ-unsaturated phosphines has shown[142] that the multiple bond is not involved, and as a result previously unknown unsaturated phosphinimines are formed.

2. Isocyanatophosphines and Methyleneaminophosphines

Three-coordinated phosphorus compounds containing an αβ-N=C bond react as 1,3-dipoles with nitrilimines, according to a 3 + 3 → 6 scheme similarly to alkenyl- and alkynyl-phosphines. Reaction between isocyanatodiphenylphosphine and a nitrilimine yields a cyclic ketoiminophosphorane independently of the nature of the substituents in the nitrilimine[143,144]:



The course of the reaction supports the above two-stage nucleophilic mechanism of interaction between αβ-unsaturated compounds of tervalent phosphorus and 1,3-dipolar systems[141]. Diphenylmethyleneaminodiphenylphosphine, in contrast to the isocyanate, reacts with *C*-ethoxycarbonyl- and *C*-acetyl-*N*-arylnitrilimines to form open-chain azomethylenephosphoranes[145].

Thus 1,3-dipolar cycloaddition of organophosphorus compounds provides a convenient method for synthesising phosphorus-containing heterocycles, which find widespread use in many branches of the national economy—as medicinals, as insecticides in agriculture, and as polymerisation initiators in chemical industry. Investigation of such reactions broadens our ideas on the influence of substituents in ligands on the dipolarophilic activity of a multiple bond, the factors determining the reactivity of dipole–dipolarophile systems, and the mechanism of cycloaddition reactions.

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Organic Monothiopyrophosphates

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The present state of the chemistry of organic monothiopyrophosphates is described. Discussion of methods of preparation is followed by consideration of physical and chemical properties. Close attention is paid to symmetrical monothiopyrophosphates and their isomerisation, as well as the properties distinguishing them from the unsymmetrical isomers. A list of 72 references is included.

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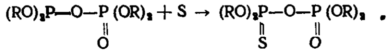
I. INTRODUCTION

Isomeric monothiopyrophosphoric acids $H_4P_2O_6S$, in contrast to pyrophosphoric (diphosphoric) acid $H_4P_2O_7$, are unknown in the free state. However, their esters are known, as well as structural analogues containing a direct carbon–phosphorus bond. The present Review covers the chemistry of monothiopyrophosphoric esters, in whose molecules the sulphur atom is located either symmetrically or unsymmetrically

which we shall term symmetrical or unsymmetrical monothiopyrophosphates. Such compounds merit special attention because of the diversity of their chemical reactions and their great practical value. They are also of theoretical interest. An existing review[1] covering the development of the chemistry of organic monothiopyrophosphates has already become insufficiently exhaustive.

II. METHODS OF PREPARATION

Tetraethyl thiopyrophosphate was first obtained in 1931 by A.E. and B.A. Arbuzov[2], by the addition of sulphur to the mixed anhydride of diethyl hydrogen phosphite and diethyl hydrogen phosphate:

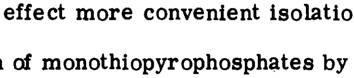


$$(RO)_2P{-}O{-}\underset{\overset{\|}{O}}{P}(OR)_2 + S \rightarrow (RO)_2\underset{\overset{\|}{S}}{P}{-}O{-}\underset{\overset{\|}{O}}{P}(OR)_2\,,$$

R=Et (I)

An unsymmetrical structure was ascribed to compound (I).

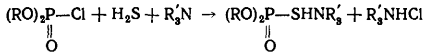
Many fresh attempts to prepare monothiopyrophosphates began two decades later. A large group of methods developed earlier were based on the phosphorylation, usually by means of dialkyl phosphorochloridates, of inorganic and organic salts of dialkyl phosphorothionates[3-6]:



$$(RO)_2\underset{\overset{\|}{S}}{P}{-}OM + Cl{-}\underset{\overset{\|}{O}}{P}(OR)_2 \rightarrow (I) + MCl\,. \qquad (1)$$

The reactions are conducted with the sodium, potassium, and ammonium salts in aprotic solvents. The method was modified[7] to effect more convenient isolation of the final product.

The formation of monothiopyrophosphates by the action of hydrogen sulphide on dialkyl phosphorochloridates in the presence of bases[8,9] can be regarded as a two-stage process. In the rate-determining first stage a salt of dialkyl hydrogen phosphorothionate (II) appears:

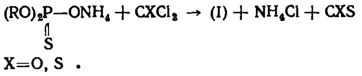


$$(RO)_2\underset{\overset{\|}{O}}{P}{-}Cl + H_2S + R'_3N \rightarrow (RO)_2\underset{\overset{\|}{O}}{P}{-}SHNR'_3 + R'_3NHCl\,.$$

(II)

In the second stage this salt (II) undergoes phosphorylation as in Eqn. (1).

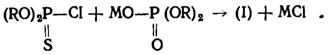
Tetra-alkyl thiopyrophosphates (I) were obtained by the action of carbonyl or thiocarbonyl chloride on ammonium dialkyl phosphorothionates[1,10-12]:



$$(RO)_2\underset{\overset{\|}{S}}{P}{-}ONH_4 + CXCl_2 \rightarrow (I) + NH_4Cl + CXS$$

$$X{=}O, S\,.$$

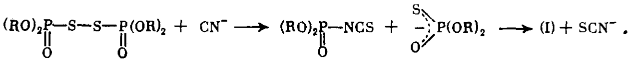
The mechanism of this reaction has not yet been adequately elucidated. An analogous method is based on the thiophosphorylation of dialkyl hydrogen phosphates or their salts[9]:



$$(RO)_2\underset{\overset{\|}{S}}{P}{-}Cl + MO{-}\underset{\overset{\|}{O}}{P}(OR)_2 \rightarrow (I) + MCl\,.$$

This reaction provides indirect evidence of the unsymmetrical structure of (I).

The reaction between the diphosphoryl disulphides (III) and potassium cyanide requires separate discussion[13]. These disulphides (III) are readily formed by the oxidation of salts of dialkyl hydrogen phosphorothioates[14], so that this method has preparative value. Investigations in our laboratory[15] on the preparation and chemistry of organophosphorus thiocyanates indicate a two-stage reaction:

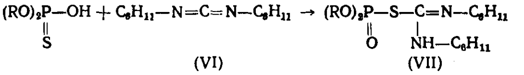


$$(RO)_2\underset{\overset{\|}{O}}{P}{-}S{-}S{-}\underset{\overset{\|}{O}}{P}(OR)_2 + CN^- \longrightarrow (RO)_2\underset{\overset{\|}{O}}{P}{-}NCS + {}^{S}_{O}{\rangle}P(OR)_2^{-} \longrightarrow (I) + SCN^-\,.$$

(III) (IV) (V)

The extremely unstable intermediate thiocyanate is converted into the isothiocyanate (IV), which then reacts with the dialkyl phosphorothioate anion (V) formed at the same time. An analogy is clearly evident between this reaction and the phosphorylation of phosphorothioic acids in conformity with Eqn. (1).

The condensation of dialkyl hydrogen phosphates with dicyclohexylcarbodi-imide (VI) [9] is the same type of reaction. It involves initial formation of the intermediate adduct (VII):[16]

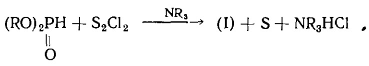


$$(RO)_2\underset{\overset{\|}{S}}{P}{-}OH + C_6H_{11}{-}N{=}C{=}N{-}C_6H_{11} \rightarrow (RO)_2\underset{\overset{\|}{O}}{P}{-}S{-}\underset{\overset{|}{NH-C_6H_{11}}}{C}{=}N{-}C_6H_{11}\,.$$

(VI) (VII)

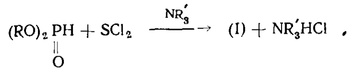
In the second stage this adduct (VII) phosphorylates another molecule of the phosphorothioate.

Two additional methods for obtaining tetra-alkyl thiopyrophosphates must be mentioned. The first is based on reaction between a dialkyl phosphite and sulphur monochloride in the presence of an amine[17-19]:



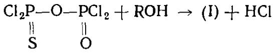
$$\underset{\overset{\|}{O}}{(RO)_2PH} + S_2Cl_2 \xrightarrow{NR_3} (I) + S + NR_3HCl\ , \qquad (2)$$

The final product is isolated from the reaction mixture by distillation. In the second method sulphur dichloride is used in the presence of a tertiary amine[18-23]:



$$\underset{\overset{\|}{O}}{(RO)_2PH} + SCl_2 \xrightarrow{NR'_3} (I) + NR'_3HCl\ , \qquad (3)$$

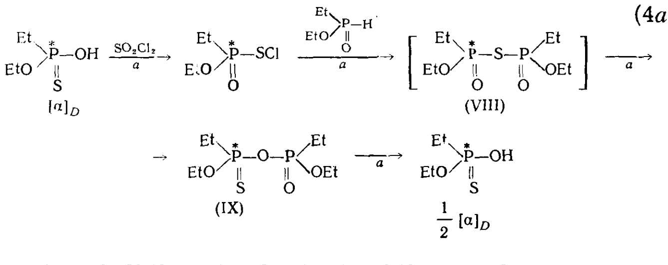
The dichloride and the amine can be replaced by the dialkylaminosulphenyl chloride R'_2NSCl.[20,21] Present-day knowledge indicates that the primary product of reaction (2) is the diphosphoryl disulphide (III), which breaks down with formation of an unsymmetrical thiopyrophosphate[24]. Reaction (3) involves initial formation of a symmetrical thiopyrophosphate, which in the presence of the amine and at a higher temperature is converted into an unsymmetrical isomer. A special method for obtaining an unsymmetrical thiopyrophosphate, in which the PS.O.PO group of the initial product remains undisturbed, is alcoholysis of thiopyrophosphoric tetrachloride[25]:



$$\underset{\overset{\|}{S}}{Cl_2P}—O—\underset{\overset{\|}{O}}{PCl_2} + ROH \rightarrow (I) + HCl$$

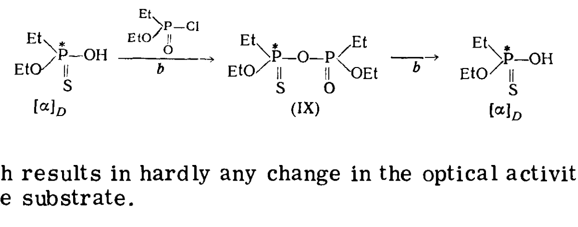
which is accompanied by alcoholysis of the P-O-P bond.

Thermochemical estimates indicate that in thiopyrophosphates the unsymmetrical skeleton is more stable than the symmetrical skeleton by ~35 kJ mole^{-1}.[26] This suggested that thiopyrophosphates containing a P-S-P group should be sufficiently stable to be isolated. In 1962 application of a stereochemical method proved[27,28] that an intermediate product containing this group is formed in the reaction between an optically active chlorothio-alkylphosphinic ester and an alkylphosphinic ester. The series of reactions



(4*a*)

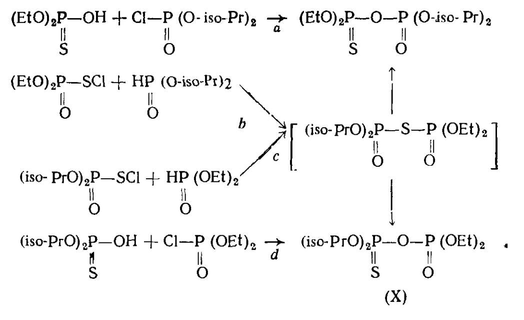
leads to half the optical activity of the initial phosphonothioic ester. Such an experimental result can be explained only by formation of the symmetrical bond system (O)P-S-P(O) in the intermediate product (VIII), which is then converted into the product (IX). This conclusion is supported by the series of reactions



(4*b*)

which results in hardly any change in the optical activity of the substrate.

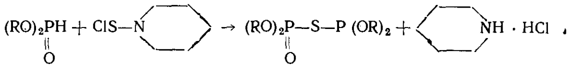
Proof of the intermediate formation of a symmetrical thiopyrophosphate was obtained by investigating the reactions of dialkyl *S*-chlorothiophosphonates with dialkyl phosphites[29]



(5)

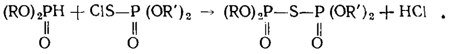
The final product of reactions (5*b*) and (5*c*) is always an unsymmetrical thiopyrophosphate (X). This provides convincing support for the view that reactions (5*a*) and (5*d*)—the phosphorylation of dialkyl hydrogen phosphorothioates by means of dialkyl phosphorochloridates according to scheme (1)—leads directly to the formation of a P-O-P bond without intermediate formation of a product having a symmetrical skeleton.

It was subsequently established[23] that symmetrical thiopyrophosphates are formed in the reaction of a dialkyl *S*-chlorothiophosphonate with a dialkyl phosphite[23]. A general method was the reaction of dialkyl phosphites with piperidinosulphenyl chloride (XI),[23,30] yielding symmetrical thiopyrophosphates containing four identical substituents:



(XI)

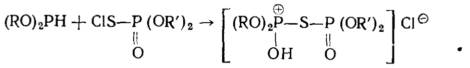
A more general method is use of the dialkyl *S*-chlorothiophosphonate (XII),[31,32] which enables different substituents to be attached to the different phosphorus atoms:



$$\underset{\overset{\|}{O}}{(RO)_2PH} + ClS—\underset{\overset{\|}{O}}{P}(OR')_2 \rightarrow \underset{\overset{\|}{O}}{(RO)_2P}—S—\underset{\overset{\|}{O}}{P}(OR')_2 + HCl\ .$$

(XII)

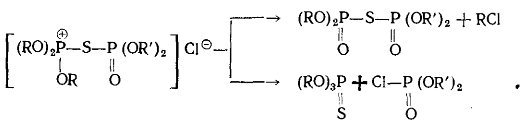
These reactions are probably of the Arbuzov type[28,30-32] with formation of an intermediate phosphonium complex:



$$\underset{\overset{\|}{O}}{(RO)_2PH} + ClS—\underset{\overset{\|}{O}}{P}(OR')_2 \rightarrow \left[(RO)_2\underset{\overset{|}{OH}}{\overset{\oplus}{P}}—S—\underset{\overset{\|}{O}}{P}(OR')_2\right]Cl^{\ominus}\ .$$

(XIII)

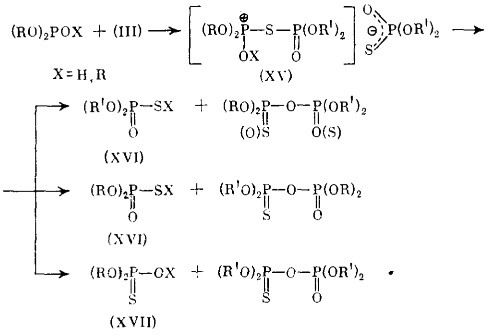
This complex (XIII) breaks down to form a symmetrical thiopyrophosphate and hydrogen chloride. The use of trialkyl phosphites (RO)$_3$P instead of dialkyl phosphites (RO)$_2$POH may change the mode of decomposition of the complex (XIV):[31]



(XIV)

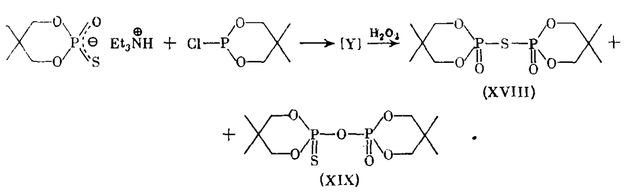
In such a case the symmetrical thiopyrophosphate is accompanied by the corresponding trialkyl phosphorothionate and dialkyl phosphorochloridate.

A special group of reactions for obtaining monothiopyrophosphates involve the diphosphoryl disulphides (III) with dialkyl[33,34] or trialkyl[35] phosphites. At present it is thought most probably that the reaction mechanism involves intermediate formation of a phosphonium complex (XV):



If in (XV) the substituent X = H, the cation of the complex (XV) is identical with the cation of the compound, and decomposition of (XV) yields a symmetrical thiopyrophosphate. If X = Alk, the cation (XV) contains three electrophilic centres—the substituent X and the two phosphorus atoms—with the occurrence of three parallel substitutions by an anion, since dialkylation of the cation (XV) is slower than deprotonation of the cation (XIII). The substitution products when X is an alkyl group are a trialkyl phosphorothioate (XVI) and two isomeric unsymmetrical thiopyrophosphates formed by isomerisation of the symmetrical skeleton. Two other reactions result from substitution by an anion at the two phosphorus atoms: substitution at the phosphonium atom P^+ yields a trialkyl phosphorothiolate (XVI) and an unsymmetrical thiopyrophosphate, whereas substitution at the phosphorus atom of the phosphinyl group leads to formation of a trialkyl phosphorothionate (XVII) and an unsymmetrical thiopyrophosphate containing four identical substituents. The action of triphenylphosphine on di(5,5-dimethyl-2-oxo-1,3,2-dioxaphosphorinan-2-yl) disulphide follows a similar course[36] to give an unsymmetrical thiopyrophosphate and a dithiopyrophosphate.

The first stable symmetrical monothiopyrophosphate to be synthesised was di-5,5-dimethyl-2-oxo-1,3,2-dioxaphosphorinan-2-yl sulphide (XVIII), obtained from an ammonium phosphorothioate and a phosphorochloridite[37]:



Three isomeric structures—essentially PO.S.P, PO.PS, and PS.O.P—can be suggested[38] for the unidentified unstable product Y obtained in the first stage. Oxidation of Y directly after formation gives a symmetrical thiopyrophosphate (XVIII), whereas oxidation of Y after storage yields an unsymmetrical thiopyrophosphate (XIX). The original attempts to obtain symmetrical thiopyrophosphates by oxidising compounds containing a P.S.P group always resulted in an unsymmetrical isomer[39,40].

Methods for obtaining thiopyrophosphates can in general be divided into two groups, comprising those leading directly to unsymmetrical products and those in which symmetrical thiopyrophosphates are formed, at least as intermediate products. The phosphorylation of dialkyl hydrogen phosphorothioates and the thiophosphorylation of dialkyl hydrogen phosphates by compounds such as dialkyl phosphorochloridates belong to the first group. The first or second substrate is often an intermediate formed in the reaction medium. In our view several published methods yielding thiopyrophosphates, whose mechanisms have not yet been fully investigated[18,41-45], can also be included in this group. The second group is based on the reactions of dialkyl phosphites with sulphenyl compounds. They involve an intermediate phosphonium complex and yield symmetrical thiopyrophosphates, but it is often impossible to isolate the latter from the reaction medium[18-22,31,46-49] owing to isomerisation. The presence of amines, acids, or ammonium salts, as well as an incorrect purification technique, results in rapid conversion of symmetrical into unsymmetrical products. These facts make clear why symmetrical thiopyrophosphates were exclusively obtained in much of the earlier work. Formally, the isomerisation of symmetrical into unsymmetrical thiopyrophosphates can be regarded as an effective method for obtaining the latter.

III. STRUCTURE AND PHYSICAL PROPERTIES

Tetra-alkyl monothiopyrophosphates are oily, non-volatile liquids, readily soluble in organic solvents but sparingly soluble in water. Several of them, e.g. derivatives of neopentyl glycol and alcohol, are crystalline.

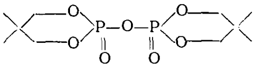
The intense biological activity of unsymmetrical thiopyrophosphates has been known for a long time: they are poisons, blocking the choline esterase system[50,51]. In view of the strong phosphorylating properties of symmetrical thiopyrophosphates, they may also be expected to possess high biological activity. Caution must be exercised in working with thiopyrophosphates.

Spectral and several other properties of monothiopyrophosphates have been reported[30-32], among which the infrared and phosphorus-31 nuclear magnetic resonance spectra are most characteristic. The infrared spectra of symmetrical thiopyrophosphates contain an absorption band in the range 520–545 cm^{-1}, corresponding to vibrations of P–S–P bonds. The characteristic band of the P=O group appears at 1270–1315 cm^{-1}, at lower wavenumbers for symmetrical thiopyrophosphates. Bands due to the P=S and P–O–P groups in unsymmetrical thiopyrophosphates are less intense, and usually appear in the region of deformation vibrations of the bonds of alkyl substituents.

As can be predicted, the signals of phosphorus nuclei in the ^{31}P n.m.r. spectrum of monothiopyrophosphates have the form, after the spin interaction of phosphorus and hydrogen nuclei has been decoupled, of pairs of separate singlets. The spectra of symmetrical thiopyrophosphates having four identical substituents contain ^{31}P n.m.r. singlet signals. The chemical shift relative to orthophosphoric acid of the phosphoryl group in symmetrical thiopyrophosphates lies between −15 and −5 ppm. In the spectra of unsymmetrical thiopyrophosphates the chemical shifts of phosphoryl and thiophosphoryl groups are respectively +12–25 and −55 to −40 ppm.[52,53]

Infrared[9,54] and Raman[55] spectra have been used to confirm unsymmetrical structures. At the present time the most convenient method of structure investigation and identification of thiopyrophosphates is ^{31}P supplemented by ^{1}H n.m.r. spectroscopy. Recently, unsymmetrical tetraethyl monothiopyrophosphate has been used to investigate the structure of organic compounds by means of the Faraday effect[56].

Table 1 lists results of the X-ray examination of the lattice structure[57] of the cyclically substituted monothiopyrophosphates (XVIII) and (XIX) together with the analogous cyclic pyrophosphate.



(XX)

Table 1. Crystallographic data for 2,2-dimethyltrimethylene pyrophosphate and monothiopyrophosphates[57].

Ester	Space group	Parameters of unit cell				X-ray density, g cm^{-3}
		No. of mol.	lattice constants, Å			
			a	*b*	*c*	
(XVIII)	***Pbca***	4	18.66	9.25	9.05	1.40
(XIX)	*Pbca*	8	27.96	9.84	11.28	1.41
(XX)	*Pbca*	8	26.90	10.00	11.13	1.39

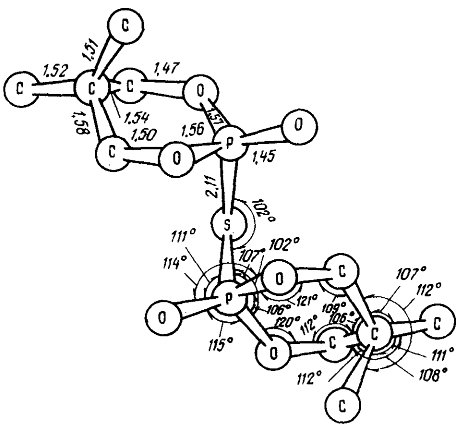


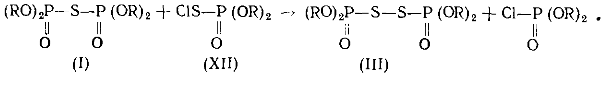
Figure 1. Structure of a molecule of symmetrical bis-2,2-dimethyltrimethylene thiopyrophosphate (XVIII) in the crystal.

The unsymmetrical thiopyrophosphate (XIX) and the pyrophosphate form isostructural crystals in the form of rhombic bipyramids. The symmetrical thiopyrophosphate (XVIII) also has a rhombic lattice, but with different symmetry and unit cell parameters. The molecule of (XVIII), who structure in the crystal[58] is illustrated in Fig. 1, differs from the pyrophosphate[59] and the unsymmetrical thiopyrophosphate in having a twofold symmetry axis lying in the plane of the P–S–P bond system and passing through the central sulphur atom. It is characterised by long P–S bonds and relatively remote oxygen atoms in the P=O groups. The dioxaphosphan rings are flatter than the cyclohexane ring. Such flattening is exhibited by other dioxaphosphans[59, 60]. The central sulphur atom in this symmetrical molecule, like the central oxygen atom in the pyrophosphate, occurs in the crystal in an axial position[58, 59] with respect to the principal plane of the dioxaphosphan rings. In solution this molecular structure of (XVIII) is probably atypical, since the ^1H n.m.r. spectra of solutions indicate an equatorial arrangement[61] of the sulphur atom.

IV. CHEMICAL PROPERTIES

Tetra-alkyl monothiopyrophosphates contain three types of reactive centres—electrophilic phosphorus and carbon atoms and the nucleophilic sulphur atom—so that this group of compounds is characterised by three types of reactions. The chemical properties of organic monothiopyrophosphates are determined mainly by the presence around the phosphorus atoms of two strong electrophilic centres and "good" leaving groups. In this sense thiopyrophosphates resemble their oxygen analogues—pyrophosphates.

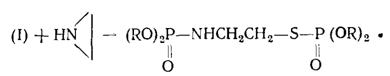
Examples of reactions in which nucleophilic properties are developed are that of an unsymmetrical thiopyrophosphate with elementary chlorine, giving a mixture of products containing the P-SCl group, and the slow reaction of a symmetrical thiopyrophosphate with the dialkyl *S*-chlorothiophosphonate (XII), yielding the diphosphoryl disulphide (III) [32]



$$\underset{(I)}{(RO)_2\overset{O}{\overset{\|}{P}}{-}S{-}\overset{O}{\overset{\|}{P}}(OR)_2} + \underset{(XII)}{ClS{-}\overset{O}{\overset{\|}{P}}(OR)_2} \rightarrow \underset{(III)}{(RO)_2\overset{O}{\overset{\|}{P}}{-}S{-}S{-}\overset{O}{\overset{\|}{P}}(OR)_2} + Cl{-}\overset{O}{\overset{\|}{P}}(OR)_2 .$$

Alkylating properties may appear at the carbon atoms of a thiopyrophosphate during nucleophilic substitution. Such reactions have not been investigated systematically, but after an unsymmetrical thiopyrophosphate has been stored or heated the corresponding phosphates, thiophosphates, and polymeric products are detected[9].

The addition of aziridine to the P–S–P chain in thiopyrophosphates, yielding diphosphorylated derivatives of 2-aminoethanethiol, has recently been described in the patent literature[62]. In the case of a symmetrical thiopyrophosphate the course of the reaction is



$$(I) + HN\!\!<\!|\; \rightarrow (RO)_2\overset{O}{\overset{\|}{P}}{-}NHCH_2CH_2{-}S{-}\overset{O}{\overset{\|}{P}}(OR)_2 .$$

The first stage probably involves nucleophilic substitution at the phosphorus atom; after this the anion of phosphorothioic acid adds to the aziridine residue.

From the difference in energy between the O–P and S–P bonds in the thiopyrophosphate skeletons[26, 63] we may predict that symmetrical isomers will react more vigorously than unsymmetrical isomers in reactions of a phosphoryl centre with nucleophilic compounds. This represents an interesting case of the presence of a leaving group, which is a "better" group not only because of the stability of the anion formed but also because the energy of the ruptured bond is less.

In symmetrical monothiopyrophosphates two phosphoryl groups are the reaction centres. Their relative reactivity depends solely on the nature of the substituents attached to the phosphorus atom. The unsymmetrical isomers contain two different groups—phosphoryl and thiophosphoryl—of which the former undergoes nucleophilic substitution more rapidly[37, 64]. Reaction on the latter centre can be observed provided that the reactivity of the former is diminished by appropriate choice of substituents; such diminution may be accomplished also by the type of nucleophilic reagent employed[65].

An unsymmetrical thiopyrophosphate undergoes hydrolysis almost exclusively at the phosphoryl centre. Kinetic data[66] for the hydrolysis of tetraethyl pyrophosphate and the corresponding unsymmetrical thiopyrophosphate indicate that the presence of the sulphur atom in the latter has relatively little effect on the reactivity of the phosphoryl centre (Table 2). Comparison of kinetic results for the hydrolysis of mono- and di-thiopyrophosphates[67, 68] confirm (Table 2) the lower reactivity of the thiophosphates found with trisubstituted phosphates and phosphorothioates[69, 70].

Table 2. Rates of hydrolysis of tetraethyl pyrophosphate, unsymmetrical thiopyrophosphate, and dithiopyrophosphate.

Compound	Aqueous solvent (dioxan, %)	Hydrolysis rate const. 10^5k, s^{-1}	Arrhenius activation parameters		Ref.
			E, kJ mole^{-1}	lg A	
$(EtO)_2\underset{\underset{O}{\|}}{P}-O-\underset{\underset{O}{\|}}{P}(OEt)_2$	0	41.0*	44.0	3.12	66
$(EtO)_2\underset{\underset{S}{\|}}{P}-O-\underset{\underset{O}{\|}}{P}(OEt)_2$	0 50	21.8 2.53	51.9 67.8	4.02 5.43	66 67
$(EtO)_2\underset{\underset{S}{\|}}{P}-O-\underset{\underset{S}{\|}}{P}(OEt)_2$	50	0.85	116.9	12.18	68

* Calculated by means of the Arrhenius equation.

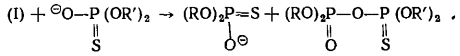
Table 3. Kinetic data for the alkaline and acid hydrolysis of unsymmetrical tetraethyl monothiopyrophosphate at 25°C.[66]

Solvent	$10^5 k$	Arrhenius activation parameters	
		E, kJ mole^{-1}	lg A
Water	0.82 s^{-1}	51.9	4.02
KOH, 0.02 M	9600 M^{-1} s^{-1}	50.6	7.86
HCl, 5.78 M	1.19 s^{-1}	75.8	8.35

Hydrolysis of tetraethyl monothiopyrophosphate is considerably more rapid in alkaline than in neutral medium, while the catalytic effect of acids is insignificant. Table 3 gives some kinetic data for this process. The mechanism of the reaction is explained on the basis of specific acid–base catalysis.

The reactivities of symmetrical and unsymmetrical thiopyrophosphates have been compared[71] with respect to neutral hydrolysis in aqueous dioxan solution with the cyclic compounds (XVIII) and (XIX) as examples. The two compounds yield identical organic phosphoric and phosphorothioic acids as hydrolysis products. The rate of reaction of the symmetrical isomer exceeds that of the unsymmetrical isomer approximately hundredfold (Table 4). The reaction velocity is influenced significantly by solvation[67, 71], whose role is indicated by a difference for these isomers in the dependence of the hydrolysis rate constant on the dioxan content of the solvent (Fig. 2).

An interesting reaction is the nucleophilic substitution of a symmetrical thiopyrophosphate by the dialkyl phosphorothioate anion[32], in which an unsymmetrical isomer is formed with regeneration of the nucleophilic reagent:



$$(I) + {}^{\ominus}O-\underset{\underset{S}{\|}}{P}(OR')_2 \rightarrow (RO)_2\underset{\underset{O^{\ominus}}{|}}{P}{=}S + (RO)_2\underset{\underset{O}{\|}}{P}-O-\underset{\underset{S}{\|}}{P}(OR')_2\ .$$

Table 4. Rates of hydrolysis of symmetrical and unsymmetrical thiopyrophosphates in aqueous dioxan at 80°C.[71]

Compound	Dioxan mole fraction	$10^5 k$, s^{-1}	Arrhenius activation parameters		Compound	Dioxan mole fraction	$10^5 k$, s^{-1}	Arrhenius activation parameters	
			E, kJ mole^{-1}	lg A				E, kJ mole^{-1}	lg A
(XVIII)	0.2	103*	66.5	6.89	(XIX)	0.2	0.52	69.1	5.05
(XVIII)	0.6	17*	58.2	4.84	(XIX)	0.6	0.072	71.2	8.33

* Calculated by means of the Arrhenius equation.

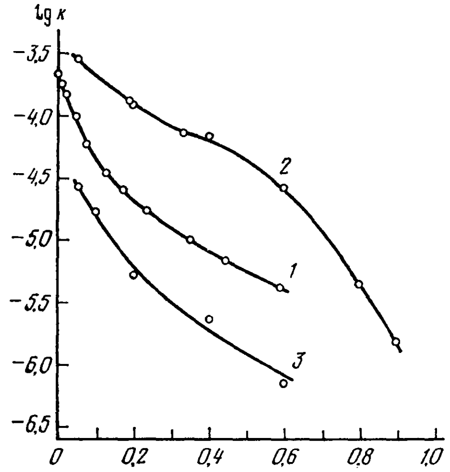
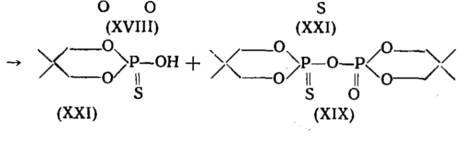


Figure 2. Dependence of hydrolysis rate constant on mole fraction of dioxan in aqueous solvent: 1) unsymmetrical tetraethyl thiopyrophosphate (80°C);[67] 2) symmetrical thiopyrophosphate (XVIII) (50°C);[71] 3) unsymmetrical thiopyrophosphate (XIX) (80°C).[71]

The reaction is bimolecular, but if the two reagents have the same substituents (R = R′) the reaction velocity is described by a first-order kinetic equation. Activation parameters for the reaction of the symmetrical thiopyrophosphate (XVIII) with the acid ester (XXI)[72]



have been determined as $\Delta H^{\neq} = 69$ kJ mole^{-1} and $S^{\neq} = -74$ J mole^{-1} deg^{-1}. The reaction is accelerated in the presence of amines. The above reactions most probably occur when contaminated specimens of symmetrical thiopyrophosphates are stored, and lead to spontaneous isomerisation of the latter.

The thermal isomerisation of a symmetrical thiopyrophosphate, which may proceed in parallel with the above reaction with an organic phosphorothioic acid, is unimolecular. The thermodynamic parameters of this reaction have been determined for the symmetrical (XVIII) in a polar solvent as $\Delta H^{\neq} = 128$ kJ mole^{-1} and $\Delta S^{\neq} = -16$ J mole^{-1} deg^{-1}. The transition state is probably amphoteric in structure.

Our kinetic investigations and certain qualitative results suggest that unsymmetrical are formed from symmetrical thiopyrophosphates by two independent reactions—unimolecular thermal isomerisation and bimolecular nucleophilic substitution.

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Optical Isomers in Solution Investigated by Nuclear Magnetic Resonance

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Work during recent years on the n.m.r. spectroscopy of solutions of optical antipodes and their mixtures with each other and with epimers is surveyed. The phenomenon of statistically controlled anisochronism of diastereomeric association (SCADA) is described. Several factors—the nature of the stereoisomers, the solvent, the temperature, etc.—affect the multiplicity of the diastereomeric anisochronism spectra. The above phenomenon is not observed in the absence of association. A theory of the phenomenon is given, and theoretical calculations are compared with experimental results. A list of 41 references is included.

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I. INTRODUCTION

Aspects of the stereoselectivity of the molecular association of optical antipodes in solution have recently been attracting the attention of research workers. They are closely connected with the problem of the existence of racemic compounds in solution and in the liquid phase in general. There are a large number of papers and many reviews on this topic (for an excellent review see Ref. 1). Differences in the interactions of identical chiral molecules (e.g. S...S or R...R) or of antipodal molecules (i.e. S...R) have been studied theoretically by quantum-chemical methods [2] and in terms of the three-body problem [3]. Spatial relations were taken into account in applying statistical thermodynamics [4]. A similar treatment has been made to the classic approximation [5].

Experimental methods for studying the association of chiral molecules—measurement of density, molecular mass, viscosity, dipole moments, surface tension, heats of mixing, refractive indices of solutions, absorption spectra, etc.[1]—have not given unambiguous results. Polarimetric investigations have given more precise information. Horeau [6] was the first to show that the optical purity P of a mixture of antipodes of $\alpha\alpha$-ethylmethylsuccinic acid $HO.CO.CH_2.C(CH_3)(C_2H_5).COOH$ may vary non-linearly with the enantiomeric purity Q. Here

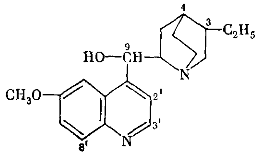
$$P = [\alpha]_\lambda^t/[\alpha_0]_\lambda^t; \quad Q = ([D]-[L])/([D]+[L])$$

where $[\alpha]_\lambda^t$ and $[\alpha_0]_\lambda^t$ are the angles of rotation of the mixture and of an optically pure specimen, while [D] and [L] are the corresponding concentrations of the antipodes in the mixture. Horeau attributed this non-linearity to different contributions by diastereomeric association complexes to the observed angle of rotation of the plane of polarisation, which served as basis for using polarimetry to investigate the interaction of antipodes in solution.

The nuclear magnetic resonance method occupies a special place in these investigations. The reason is that separate signals for diastereomeric forms can be observed in n.m.r. spectra. It has been known for a long time that the n.m.r. spectra of diastereomers may differ in the chemical shifts of signals from indicator nuclei [7,8], and this difference has been termed *diastereomeric anisochronism*. Quite recently it has become known that such anisochronism can be observed in solutions not only of diastereomeric molecules but also of diastereomeric association complexes of enantiomers, even with rapid exchange between the complexes (see below). Diastereomeric anisochronism has two independent parameters—the diastereomeric chemical shift, determined by spatial independent differences in the chemical environment of the indicator nucleus in the diastereomers, and the relative integral intensity in the diastereomeric doublets, representing the relative content of the given diastereomeric form in the solution.

We are thus concerned with the laws of diastereomeric anisochronism—the magnetic non-equivalence of nuclei in diastereomeric systems—in the narrow sense in diastereomeric molecules [7,8]; spectra of this kind are used to determine absolute configuration [9] and enantiomeric purity [10]. It includes also diastereomeric anisochronism of enantiomers in chiral solvents [11] or in achiral solvents but in the presence of chiral additives [12], which in particular may even be chiral shift reagents [12]. Finally, it includes the dynamic anisochronism of enantiomers in achiral solvents when the concentrations of the enantiomers are unequal, which is the type that will be surveyed in the present Review.

In 1969 Williams et al. [13] found that the multiplicity of the spectrum of a 1 : 1 mixture of racemic and optically active *laevo*-dihydroquinine was doubled in an achiral solvent. They felt it necessary, of course, to compare the ^1H n.m.r. spectrum (in deuterochloroform) of the racemic dihydroquinine

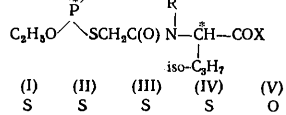


obtained on repeating Rabe's well known multistage synthesis, with the spectrum of natural (−)-dihydroquinine. The comparison showed that the signals from protons 2′, 3′, 8′, and 9 did not coincide but differed by 0.1 − 0.2 ppm. The spectrum of 1 : 1 mixture of racemic and optically active dihydroquinines showed a doubled multiplicity of these signals. The intensity ratio of the components of the doublets was 3 : 1, which corresponded to the concentration ratio of (−)- and (+)-dihydroquinines. The effect diminished on dilution and on replacement of deuterochloroform by deuteromethanol as solvent, and it decreased substantially when the hydroxy-group was acetylated. These observations were correctly interpreted[13] as evidence that, in a solution of the pure enantiomers, the racemate, and their mixtures, molecules of each individual enantiomer are situated in an identical environment, enantiomeric and diastereomeric respectively.

In a series of publications the Reviewers have reported an analogous phenomenon and a detailed study[15-20] of solutions of compounds containing two chiral centres, of the type $C_2H_5O.\overset{*}{P}O(CH_3).S.CH_2.CO.NH.\overset{*}{C}HR.COOH$. At the same time an axiomatic theory was constructed for the spectra of states of diastereomeric systems that were due to the stereospecificity of interaction of their chiral fragments[21]. One deduction from this theory was the theoretical possibility that the multiplicity of the diastereomeric anisochronism spectra of solutions of enantiomers in an achiral medium would be increased with a non-racemic concentration ratio of the antipodes. The effects studied by Williams et al.[13] indicated that the diastereomeric anisochronism observed in these cases was due to the short lifetime of association complexes of chiral molecules with rapid exchange between the complexes, i.e. with statistical control of the system. The phenomenon of the n.m.r. non-equivalence of enantiomers, occurring in such systems in an achiral medium with rapid averaging due to exchange between association complexes, has been termed *statistically controlled anisochronism of diastereomeric association* (SCADA). This is a physical aspect of statistically controlled diastereomeric association. The experimental and theoretical results of research on the former phenomenon discussed below throw light on interesting features of the latter phenomenon.

II. DIASTEREOMERIC ANISOCHRONISM IN ORGANOTHIOPHOSPHORUS DEPSIPEPTIDES

Studies of mixtures of stereoisomers of *P*-ethoxy-*P*-methylphosphinothioylthiologlycolloylvaline (I), its ethyl ester (II), the corresponding *N*-methylated derivatives (III) and (IV)



$$CH_3(C_2H_5O)\overset{*}{P}(=Y)SCH_2C(O)N(R)-\overset{*}{C}H(iso\text{-}C_3H_7)-COX$$

Compound	(I)	(II)	(III)	(IV)	(V)	(VI)
Y	S	S	S	S	O	O
R	H	H	CH_3	CH_3	H	H
X	OH	OC_2H_5	OH	OC_2H_5	OH	OC_2H_5

and a few of their simpler analogues[18,19] have revealed several intramolecular factors influencing the occurrence and variation of diastereomeric anisochronism, as well as solvation effects by molecules of a magnetically anisotropic solvent. The results were in general consistent with the views of Mislow and Raban[22], although certain facts required special treatment, e.g. the phenomenon of diastereomeric anisochronism induced by aromatic solvation[17].

In the mixtures of diastereomers investigated in solution in chloroform or benzene diasteromeric anisochronism is evident in a doubling of the multiplicity of the ^1H or ^{31}P n.m.r. spectra. In the latter spectra under conditions of wide-band suppression of spin–spin interactions with protons it is apparent as a well resolved phosphorus doublet. We therefore used $^{31}P-\{^1H\}$ n.m.r. in subsequent investigations. The impetus to a more profound study of diastereomeric anisochronism spectra in these and analogous systems was provided by observation of the unusual influence of the concentration and temperature, and also mixing[7], of solutions of the diastereomers on the $^{31}P-\{^1H\}$ n.m.r. spectra both of compounds (I)–(IV) and especially of their monothio-analogues (V) and (VI).

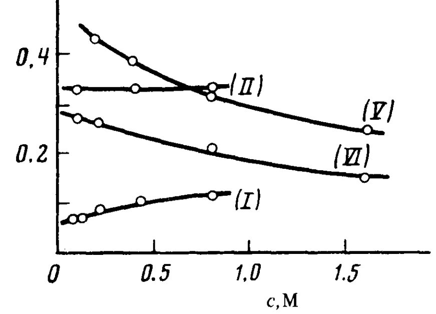


Figure 1. Concentration dependence of diastereomeric anisochronism in $^{31}P-\{^1H\}$ n.m.r. spectra of mixtures of four isomers in chloroform at 20°C (V at 25°C). The numbering of the curves corresponds to that of the compounds in the text.

The molecules of these compounds contain two asymmetric atoms—phosphorus and carbon—so that four stereoisomers—RR, SS, RS, and SR—are possible. Dilution of a chloroform solution of a specimen of the ethyl ester (II) of the dithio-derivative, which was a mixture of all four stereoisomers, had no effect at all on the diastereomeric anisochronism: the difference Δδ in the chemical shifts in the phosphorus doublet remained constant (Fig. 1). For the free acid (I) the difference diminished on dilution, which could easily be explained by the influence[23] of intermolecular hydrogen bonds on the anisochronism: dilution tends to rupture the hydrogen bonds, diminish the rigidity of the system, liberate frozen degrees of freedom, and diminish diastereomeric anisochronism by averaging.

It was found unexpectedly that dilution of solutions of the monothio-derivatives (V) and (VI) (each specimen also a mixture of four stereoisomers) produced increases in diastereomeric anisochronism, respectively strong and less marked, while the difference Δδ increased (Fig. 1). Still more complicated relations were evident with variation in temperature (Fig. 2). The dithio-derivatives (I) and (II) showed a decrease in Δδ with rise in temperature. In solutions of the monothio-derivative (V) and (VI) a rise in temperature from −60 to −45°C was accompanied by decrease in Δδ, but further rise to +50°C by a continuous increase. At about −45°C the difference Δδ became zero (or smaller than the resolving power of the instrument). Since only the absolute value was measured in such an experiment, not the sign of the difference, an alternative conclusion was that the function increased monotonically with rise in temperature from −60 to +50°C but changed sign at −45°C.[19,20]

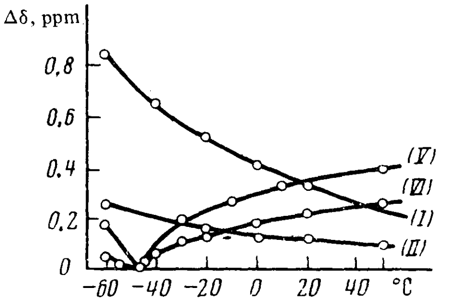


Figure 2. Temperature dependence of diastereomeric anisochronism in $^{31}P-\{^1H\}$ n.m.r. spectra of 0.4 M mixtures of four isomers in chloroform. The numbering of the curves corresponds to that of the compounds in the text.

To understand such complicated relations it is necessary to simplify the test systems consisting of mixtures of four stereoisomers (two racemic diastereomers). This was difficult with dithio-derivatives, since the phosphorus chiral centre arose at the instant of formation of the compound, but the separation of diastereomers and the resolution of racemates were quite complicated tasks. The monothio-derivative (V) provided a more favourable situation: enantiomeric (R and S) monothio-acids of phosphorus are readily available[24], as are also enantiomeric (R and S) chloroacetylvalines[25]; preparation of (V) from them leaves the centres of asymmetry unaffected, and is conducted under conditions under which no racemisation of chiral centres is observed. It thus became possible to obtain in pure form all four stereoisomers of (V)[15]—RR, SS, RS, and SR—and to investigate the $^{31}P-\{^1H\}$ n.m.r. spectra of their chloroform solutions both individually and in mixtures of various relative concentrations.

The value of Δδ calculated as the difference between the chemical shifts in the spectra of solutions of pure diastereomers of (V) taken separately was not identical with the difference in chemical shifts in solutions of mixtures of the same diastereomers at the same total concentration. In the spectra of the stereoisomers SS and SR taken separately the difference Δδ = 0.84 ppm, whereas a mixture of the same total concentration gave Δδ = 0.04 ppm, but mixing the stereoisomers SS and RS separated the signals of the doublet to Δδ = 1.05 ppm.

Furthermore, the spectrum of a mixture of all four stereoisomers in unequal concentrations contains four signals exhibiting intensity ratios equal to the corresponding concentration ratios. Finally, the temperature dependence of the spectrum of an equimolecular mixture of the four stereoisomers differs from that for the stereoisomers taken separately[20]. Fig. 3 illustrates the temperature dependence of the chemical shifts of signals due to the stereoisomers SS and SR of compound (V), together with that of $\Delta\delta = \delta_{SR} - \delta_{SS}$.

The reason for such a difference between individual stereoisomers and their mixtures with respect to the n.m.r. spectra of the solutions could only be interaction between the dissolved molecules. In solvents of low polarity, such as chloroform and tetrachloromethane, indeed, molecules of (V) are strongly associated[26]. The dithio-ester (II) is not associated at all in chloroform, and its n.m.r. spectrum exhibits no anomalous changes on dilution or change in the temperature of the solution.

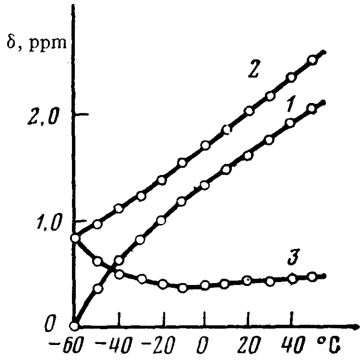


Figure 3. Temperature dependence of chemical shifts of signals from isomers of compound (V) in separate 0.4 M solutions in chloroform: 1) SS; 2) SR; 3) Δδ.

Thus the multiplicity and the frequency spacing of the signals in the diastereomeric anisochronism spectra of stereoisomers depend on association and its stereoselectivity. Hence n.m.r. spectra can be used to study the association of stereoisomers and its stereoselectivity.

III. DIASTEREOMERIC ANISOCHRONISM IN BINARY MIXTURES OF STEREOISOMERS

1. Mixtures of Enantiomers

The Reviewers investigated the n.m.r. spectra of a mixture of enantiomers of *P*-ethoxy-*P*-methylphosphinothioylthiologlycolloylvaline during 1973 and 1974.[15-18] Two fundamentally different types of association complexes of enantiomers—long and short lived—may exist with respect to the n.m.r. time scale. In the former the multiplicity of the diastereomeric anisochronism spectrum should be determined by the number of varieties of such long-lived complexes, and the intensity ratio of the signals by their relative concentrations. It would be completely fortuitous for the multiplicity to be 2 and the intensity ratio equal to the concentration ratio of the enantiomers. The other possibility—formation of short-lived association complexes with rapid exchange between them—represents the above case of statistically controlled diastereomeric association. The multiplicity of the spectrum should then be 2 (provided that the resolving power of the instrument is adequate), and the intensity ratio of the signals in an elementary doublet equal to the concentration ratio of the antipodes[16].

The $^{31}P-\{^1H\}$ n.m.r. spectrum of the enantiomers RR and SS of compound (V) in a 0.4 M solution of chloroform at −60°C contains narrow singlet signals, whose chemical shifts (homo-shifts δ_h) coincide within the limits of experimental error (±0.1 Hz). This signal will henceforward be adopted as reference point, from which other chemical shifts will be reckoned. The n.m.r. spectrum of a racemic mixture (1 : 1) of the same total concentration at the same temperature also contains a single singlet, but its position δ_r differs by 0.35 ppm (13.2 Hz) from the homo-shift δ_h. With the concentration ratio [RR] : [SS] = 7 : 3 two signals are observed, at 0.25 and 0.42 ppm, whose integral intensities are in the ratio 7 : 3. An identical spectrum is observed with the concentration ratio 3 : 7.

Similar relations are observed for the pair of antipodes RS + SR under the same conditions. At −60°C the homo-shift δ_h = 0.84 ppm, but the singlet signal of the racemic mixture is located at 0.46 ppm. Their concentration ratios 7 : 3 and 3 : 7 reveal two identical doublets at 0.38 and 0.59 ppm with the intensity ratio 3 : 7. Analogous relations are found at other temperatures. The following qualitative conclusions can be drawn from the data in Table 1.

Table 1. Chemical shifts of signals in spectra of mixtures of enantiomers of compound (V) in 0.4 M solution in chloroform (I_{rel} = relative integral intensity)*.

c_1	δ, ppm	I_{rel}	t, °C											
			−60	−50	−40	−30	−20	−10	0	10	20	30	40	50
			SS+RR											
1.00	δ_h	1	0	0	0	0	0	0	0	—	—	—	—	—
0.50	δ_r	1	0.35	0.20	0.13	0.10	0.05	0.03	0	—	—	—	—	—
0.30	δ_{SS}	0.3	0.42	0.24	0.17	0.12	0.08	0.05	0,02	—	—	—	—	—
0.30	δ_{RR}	0.7	0.25	0.13	0.09	0.06	0.03	0	0	—	—	—	—	—
			SR+RS											
1.00	δ_h	1	0.84	0.61	0,50	0.44	0.39	0.36	0,39	0.40	0.43	0,44	0.45	0.46
0.50	δ_r	1	0.46	0.21	0.10	0.03	0,07	0,13	0.18	0.22	0.26	0,32	0.36	0.41
0,30	δ_{SR}	0.3	0.38	0.10	0.00	−0.05	−0.03	0.03	0.08	0.16	0.26	0.30	0.33	0.36
0.30	δ_{RS}	0.7	0.59	0.34	0.23	0.18	0.19	0.22	0,26	0.30	0.32	0,36	0.38	0.43

*The antipodes RR and RS have signals identical with those of SS or SR in a racemic mixture and in the pure state. The quantity

$$c_1 = [SS]/([SS] + [RR]) \text{ or } c_1 = [SR]/([SR] + [RS]).$$

The homo-signal of SS molecules at the given temperature has been adopted as reference signal.

1. Narrow singlet signals are observed in solutions of individual enantiomers. Since every molecule in an association complex is surrounded solely by identical molecules, and rapid exchange takes place between complexes, local fields induced at the indicator nucleus (in the present case phosphorus) are completely averaged out, regardless of the number and stability of the various complexes. Hence the signal is a narrow singlet. Since the magnetic field is achiral, the signals of antipodes, are, of course, identical.

2. In a solution of a racemic mixture the molecules of each enantiomer are surrounded both by identical and by antipodal molecules. Homo- and cross-association may be thermodynamically either equivalent or non-equivalent. With rapid exchange between complexes the statistics of exchange results in contamination of homo-interactions by cross-interactions at each enantiomer. This changes the resultant local field at the indicator nucleus of the enantiomer molecule and hence the chemical shift of the n.m.r. signal. Since the situations for the two enantiomers have a mirror-image relation, the chemical shifts of their signals are identical, and they merge into a single signal δ_r differing from δ_h. This difference, which is termed the *deviation* $D = \delta_r - \delta_h$, is a characteristic feature of SCADA.

3. When the concentration of antipodes in the solution are unequal, they exhibit different extents of contamination of homo- by cross-interactions: if homo-association predominates at one antipode, cross-association predominates at the other. The situations are not now those of mirrow-images, and a doublet appears in the spectrum, in which the intensity ratio of the components is equal to the concentration ratio of the antipodes.

In calculating the specific form of dependence of the signals of (+)- and (−)-enantiomers, i.e. δ^+ and δ^-, on the relative concentration of the enantiomers in the mixture we must take into account the statistical averaging, with rapid exchange between complexes, of the effects of homo- and cross-interactions on the shielding of the indicator nuclei in the molecules of the antipodes. If W_+^+ is the statistical weight of the contribution to δ^+ by homo-interaction, W_+^- is that of cross-interaction, and correspondingly W_-^- and W_-^+ are the statistical weights of the contributions to δ^- by homo- and cross-interactions, the chemical shifts of the signals due to (+)- and (−)-molecules are given by the formulae

$$\delta^+ = (W_+^+\delta_h + W_+^-\delta_c)/(W_+^+ + W_+^-), \tag{1}$$

$$\delta^- = (W_-^-\delta_h + W_-^+\delta_c)/(W_-^- + W_-^+) \tag{2}$$

in which δ_h is the homo-shift, identical for the two antipodes, and δ_c the cross-shift [also identical for (+)- and (−)-molecules].

The statistical weights of the contributions by homo- and cross-interactions are determined, of course, by two factors: the relative content of antipodal molecules in the mixture can be expressed as $c = [+]/([+] + [-])$; and the stability characteristics of homo- and cross-contacts can be represented by the functions of homo- and cross-interaction energies

$$\alpha_h = A_h \exp(-E_h/kT), \tag{3}$$

$$\alpha_c = A_c \exp(-E_c/kT). \tag{4}$$

The condition of rapid exchange between association complexes is indicated by the equations

$$\alpha_h = \langle\alpha_h\rangle,\ \alpha_c = \langle\alpha_c\rangle,\ \delta_h = \langle\delta_h\rangle,\ \delta_c = \langle\delta_c\rangle, \tag{5}$$

where the symbol $\langle\rangle$ denotes averaging over all types of association complexes containing the given interaction. We can then write

$$W_+^+ = \alpha_h c,\ W_+^- = \alpha_c(1-c),\ W_-^- = \alpha_h(1-c),\ W_-^+ = \alpha_c c. \tag{6}$$

Since experimental data do not yield values of the parameters α_c and α_h but only their ratio $\alpha_c/\alpha_h = m$ representing the stereospecificity of association of the antipodes, Eqns. (1) and (2) can be finally written

$$\delta^+ = [c\delta_h + m(1-c)\delta_c]/[c + m(1-c)], \tag{7}$$

$$\delta^- = [(1-c)\delta_h + mc\delta_c]/[(1-c) + mc]. \tag{8}$$

Inspection of formulae (7) and (8) indicates that both extrema and points of inflection are absent from both δ^+-c and δ^--c curves throughout the concentration range. When $c = 0$, we find that $\delta^+ = \delta_c$ and $\delta^- = \delta_h$; and when $c = 1$, that $\delta^+ = \delta_h$ and $\delta^- = \delta_c$; in both cases only one signal is observed, since δ_c cannot be observed. When $c = 0.5$, i.e. in a racemic mixture,

$$\delta^+ = \delta^- = (\delta_h + m\delta_c)/(1 + m), \tag{9}$$

and one signal is also observed, which is displaced by the deviation relative to the homo-signal. At all other concentrations two signals should be observed. Since each belongs to a definite antipode, the ratio of the integral intensities of these signals should be $c/(1 - c)$.

For both functions $\delta^+(c)$ and $\delta^-(c)$ the curvature depends on m, i.e. on the stereospecificity of homo- and cross-interactions. If $m = 1$ (i.e. $\alpha_c = \alpha_h$), the relations become linear:

$$\delta^+ = \delta_c - (\delta_c - \delta_h)\, c, \tag{10}$$

$$\delta^- = \delta_h + (\delta_c - \delta_h)\, c. \tag{11}$$

However, the main characteristics of the phenomenon are preserved: the spectrum contains one signal when c is 0, 1, or 0.5, and two signals at all other relative concentrations. This is a very important conclusion: the appearance of two signals in the n.m.r. spectrum of a mixture of unequal concentrations of antipodes is not a consequence of stereoselectivity of association (e.g. a tendency to racemate formation) but is caused by SCADA itself.

Table 2. SCADA parameters of the enantiomeric pairs SS + RR and SR + RS of compound (V) in 0.4 M solution in chloroform*.

t, °C	−60	−50	−40	−30	−20	−60	−50	−40	−30	−20
	SS+RR					SR+RS				
δ_c	0,50	0.31	0.22	0.17	0.10	0.26	−0.07	−0.18	−0.20	−0.21
α_c/α_h	2.4	1.7	1.4	1.2	1.0	1.8	1.7	1.6	1.4	1.2

*The reference signal adopted was δ_{SS} at the given temperature.

If δ_h is adopted as reference signal, Eqns.(7) and (8) permit a simple linear transformation giving the formulae

$$\frac{1}{\delta^+} = \frac{1}{\delta_c} + \frac{1}{m\delta_c}\cdot\frac{c}{1-c}, \tag{12}$$

$$\frac{1}{\delta^-} = \frac{1}{\delta_c} + \frac{1}{m\delta_c}\cdot\frac{(1-c)}{c} \tag{13}$$

which were used to treat the experimental data in Table 1. The parameters δ_c and

$$m_{SS}^{RR} = \alpha_{SS}^{RR}/\alpha_{SS}^{SS},\ m_{SR}^{RS} = \alpha_{SR}^{RS}/\alpha_{SR}^{SR}. \tag{14}$$

were found for each temperature, where the subscript denotes the stereoisomer whose signal is under consideration, and the superscript the stereoisomer that interacts with it in the association complex. Together with experimental values of δ_c these parameters give a complete description of the diastereomeric anisochronism spectra.

Table 2 gives the SCADA parameters, which were used in Eqns.(7) and (8) to calculate the curves in Fig.4. Good agreement is evident between calculation and experiment.

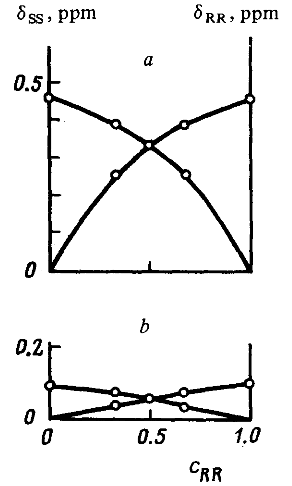


Figure 4. Dependence of chemical shifts of signals from SS and RR enantiomers of compound (V) on relative concentration of RR isomer at different temperatures: *a*) −60°C; *b*) −20°C. The curves have been obtained theoretically; the points on them represent experimental values. Each curve was reckoned from the homo-shift at the given temperature.

From the results the interesting conclusions can be drawn that for the RS + SR system the non-equivalence of shielding of the phosphorus atom in homo- and cross-complexes, i.e. $\delta_c - \delta_h$, varies comparatively slowly with rise in temperature from −60 to +50°C, while the stereoselectivity of association (the difference between m and unity) vanishes at ~0°C. In the RR + SS system both the non-equivalence of shielding and the stereoselectivity of association disappear rapidly with rise in temperature, and above 0°C the SCADA phenomenon is completely absent from the n.m.r. spectra: a single singlet signal is observed at any relative concentration of antipodes in the mixture. Thus conditions depending on the structure of the enantiomers and the thermodynamic characteristics of the system must be satisfied for SCADA to be observed in the n.m.r. spectra; otherwise the magnitude of the phenomenon in the n.m.r. will become smaller than the resolving power of the instrument. This is evidently the reason for the fewness of published examples of SCADA.

The energy difference between averaged cross- and homo-contacts in association complexes can be elucidated from the temperature dependence of α_c/α_h. Thus if

$$\alpha_c = A_c\, e^{-E_c/RT} \qquad \alpha_h = A_h\, e^{-E_h/RT},$$

we have

$$\lg(\alpha_c/\alpha_h) = \lg(A_c/A_h) + (E_h - E_c)/2.3RT.$$

A linear plot of $\lg(\alpha_c/\alpha_h)$ against $1/T$ should be observed, with a slope

$$\tan\alpha = (E_h - E_c)/2.3R,$$

whence $E_h - E_c$ can be calculated. Such linear relations are indeed found. For the pair SS + RR the difference $E_h - E_c \simeq 2$ kcal mole^{-1}, whereas the difference is ~1 kcal mole^{-1} for SR + RS. In both cases cross-interaction is appreciably more effective than homo-interaction[19,20].

A very interesting paper by Horeau and Guette[1] appeared at almost the same time as the publications by Soviet workers. As mentioned above, Horeau had earlier made a systematic study of the optical and enantiomeric purity of enantiomers. This was why he investigated the interaction of antipodes in solution and the effect of this interaction on physical constants. It has also been mentioned above that in 1969 departures from additivity were found for the angle of rotation of the plane of polarisation by solutions of a mixture of the enantiomers of α-ethyl-α-methylsuccinic acid[6]. Horeau and Guette found that such departure was still more strongly marked for solutions of the enantiomers of α-isopropyl-α-methylsuccinic acid $HO.CO.C(CH_3)(iso\text{-}C_3H_7).CH_2.COOH$ in chloroform or dichloromethane.

When discussing this result, the authors[1] refer to the work of Jurczak and Zamojski[27], who observed that the rotatory power of dimethyl malate in methanol was not a linear function of the enantiomeric composition. However, Horeau and Guette were working in non-polar solvents—chloroform and dichloromethane—and the use of methanol, ethanol, pyridine, diglyme, and acetonitrile completely depresses the non-linearity effect. Even additions of 4–6% of ethanol to chloroform were sufficient for the dependence of optical purity on enantiomeric composition to be linear. Hence it was concluded[1] that the divergence from a linear dependence of the rotatory power of a mixture of enantiomers on enantiomeric composition was due to differences in stability between diastereomeric association complexes of the antipodal molecules in the solution, so that the phenomenon could be observed only in non-ionising solvents. However, this does not extend to stable complexes, which may give deviations even in aqueous solution. Thus in the presence of ammonium molybdate $(NH_4)_6Mo_7O_{24}.4H_2O$ a solution of (+)-mandelic acid has an angle of rotation $[\alpha_0]^{22}_D = +45.6°$. For a mixture of 75% of the dextrorotatory acid and 25% of the laevorotatory acid $[\alpha]^{22}_D = -19°$. This value requires for the pure enantiomer an angle of rotation $[\alpha_E]^{22} = +38°$, instead of the observed +45.6°: i.e. non-linearity is apparent.

Table 3. Diastereomeric anisochronism in associated solutions of α-ethyl-α-methylsuccinic acid.

Substance	δ_A, Hz	$\Delta\delta_A$, Hz	δ_B, Hz	$\Delta\delta_B$, Hz	J_{AB}, Hz
Optically pure enantiomer	251,4	0	234.9	0	16.5
Mixture of antipodes	250,4	1.0	233.5	1.4	16,9
(75:25)	247,7	3,7	230,5	4.4	17.2
Racemate	248,9	2,5	231,9	3.0	17.0

However, intermolecular interactions of antipodes are most clearly indicated by results obtained by Horeau and Guette[1] in a study of the ^1H n.m.r. spectra of the above acids. These workers investigated the spectra of solutions of α-ethyl-α-methylsuccinic acid in deuterochloroform at a working frequency of 100 MHz. The protons of the methylene group give two doublets characteristic of an AB system. The magnetic non-equivalence of the two antipodes does not affect the doublet in a strong field. Table 3 gives chemical shifts and spin–spin interaction constants for the doublet in a weak field. The racemate differs appreciably in chemical shifts (by 2.5–3.0 Hz) from the optically pure enantiomers, but two signals appear in a non-equimolecular mixture of antipodes. An appreciable though smaller difference is observed for the spin–spin interaction constants. Similar results were obtained for α-isopropyl-α-methylsuccinic acid. The authors[1] interpret their findings as evidence of differences in the stability of diastereomeric interactions of enantiomers in solution.

In order to demonstrate energy differences between D...L and D...D or L...L interactions a calorimetric investigation was made[1] of solutions of enantiomers of α-ethyl(isopropyl)-α-methylsuccinic acids, and heats of mixing of antipodes at 25°C were found to be respectivelv 33.5 and 50 cal mole^{-1}. It is significant that the interaction of antipodal molecules is more advantageous energetically than is the interaction of identical molecules (this contradicts deductions made by other workers[2,3]).

Table 4. Treatment of experimental results[1,13] by means of Eqns. (12) and (13).

Enantiomers	Signal	$\delta_c - \delta_h$, Hz	α_c/α_h
Dihydroquinine	H (9)	40	1.0
α-Ethyl-α-methyl-	δ_A	−4.6	1.0
succinic acid	δ_B	−5.7	1.0

As has been shown above, diastereomeric anisochronism can be observed in solutions of enantiomers even in the absence of energy differences between homo- and cross-interactions. The appearance of an elementary diastereomeric doublet in the spectra of solutions of unequal concentrations of antipodes is due to non-equivalence of the stereochemical environment of antipodal molecules under conditions of statistical control with rapid exchange between association complexes. This non-equivalence is caused by the unequal concentration of the antipodes. It depends also, of course, on the energy parameters of association, but may arise even with equal parameters for identical and diastereomeric contacts. In this sense the conclusions of Horeau and Guette need to be refined. Equations (7) and (8) can be used to treat the experimental results for dihydroquinine[13] and α-ethyl-α-methylsuccinic acid[1]. Unfortunately, the results obtained by Williams et al.[13] are very incomplete: the authors note that the signals of aromatic protons are extremely sensitive to change in the total concentration, and coalesce on dilution. Data on the chemical shifts in the signals of 9-H protons are more reliable, their position depending mainly on the relative concentration of the antipodes. Linear plots of δ against c are obtained: i.e. stereoselectivity of association is absent. Parameters calculated by means of Eqns. (12) and (13) are listed in Table 4. Good linearity is observed also for the results of Horeau and Guette[1]. For the enantiomers of α-ethyl-α-methylsuccinic acid $m = 1$, which also supports the view that stereospecificity of association is either absent or very slight.

Thus no appreciable preference for homo- or cross-association of enantiomers is evident in solutions of dihydroquinine and of α-ethyl-α-methylsuccinic acid. In the *P*-ethoxy-*P*-methylphosphinylthiologlycolloylvalines investigated by Soviet workers cross-association, i.e. racemisation, occurs preferentially[15].

Table 5.

Amide	A	A	B	C
t, °C	15	26	15	15
δ_c	1.41	1.60	1.54	1.62
m	0,21	0.33	0.35	1.0

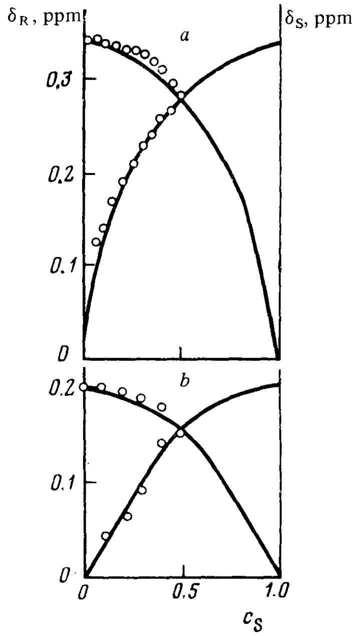
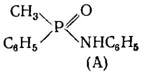
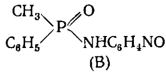
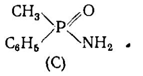


Figure 5. SCADA in deuterochloroform solution of *P*-methyl-*NP*-diphenylphosphinamide (A) at: *a*) 15°C; *b*) −26°C. The curves have been calculated theoretically; and the points represent experimental values.

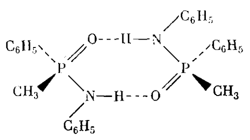
Harger[28] has investigated the ^{1}H n.m.r. spectra of amides of methylphenylphosphinic acid—the phenylamide (A), *p*-nitrophenylamide (B), and unsubstituted amide (C)

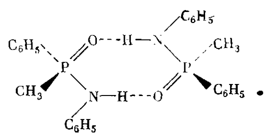

(A)


(B)


(C)

Deviation of the chemical shift for the racemic mixture of antipodes and doubling of the multiplicity of the doublet signals of *P*-methyl protons with unequal concentrations of enantiomers were observed in all cases in deuterochloroform solution. Citing Refs. 1, 13, and 15–20, Harger gives a qualitative treatment of his results that follows completely from our views. In his opinion[28] the magnetic non-equivalence of the indicator nucleus in the enantiomer molecules with statistical non-equivalence of homo- and cross-contacts and rapid exchange between complexes underlie the observed phenomenon. From infrared spectral data Harger refines the character of the diastereomeric association complexes as the dimeric


(D)


(E)

Although he gives only qualitative consideration to his results, his numerical data are susceptible to a quantitative treatment based on formulae (7) and (8). Table 5 gives values that the Reviewers have thus calculated for the SCADA parameters in the n.m.r. spectra of the phosphinamides. The curves in Fig. 5 have been calculated theoretically by the Reviewers, whereas the points have been taken from Harger's experiments[28]. It is obvious that he had investigated a typical SCADA phenomenon, with $m = \alpha_c/\alpha_h < 1$ in all cases other than the last, so that homo-association had occurred preferentially.

2. Mixtures of Epimers

Equations (1) and (2) do not involve any restrictions on the stereochemical relations of the mixture components. Equations (7) and (8), on the other hand, are applicable to mixtures only of enantiomers. If the components *i* and *j* are not antipodes but diastereomers, formulae (7) and (8) should be replaced by the more general[19,20]

$$\delta_i = \frac{\alpha_i^i c_i \delta_i^i + \alpha_i^j (1 - c_i)\, \delta_i^j}{\alpha_i^i c_i + \alpha_i^j (1 - c_i)}\,, \tag{15}$$

$$\delta_j = \frac{\alpha_j^j (1 - c_i)\, \delta_j^j + \alpha_j^i c_i \delta_j^i}{\alpha_j^j (1 - c_i) + \alpha_j^i c_i} \tag{16}$$

in which the concentrations c_i and c_j have been normalised to unity and the subscript corresponds to the isomer whose signal is under consideration, while the superscript denotes the isomer with which it interacts in the association complexes. Thus α_i^i, α_j^j and α_i^j, α_j^i are association stability characteristics; the latter two, of course, are the same for the two epimers: i.e. $\alpha_i^j = \alpha_j^i$. The chemical shifts δ_i^i and δ_j^j are homo-shifts; when $c = 1$ and $c = 0$, they equal respectively δ_i or δ_j. These shifts are unequal; furthermore $\delta_i^j \neq \delta_j^i$. In the case of enantiomers we have

$$\alpha_i^i = \alpha_j^j = \alpha_h; \quad \alpha_i^j = \alpha_j^i = \alpha_c,$$
$$\delta_i^i = \delta_j^j = \delta_h; \quad \delta_i^j = \delta_j^i = \delta_c.$$

The ^{31}P–{^{1}H} n.m.r. spectra of mixtures of epimers SS + SR and SS + RS of compound (V) were investigated. Their mirror-image mixtures RR + RS and RR + SR were enlisted only to determine the error in the measurements. Table 6 gives experimental values obtained at various relative concentrations of the epimers and of the mixture and at various temperatures. Treatment by means of formulae (15) and (16)[20] yielded all the parameters of the diastereomeric anisochronism spectra of the systems (Table 7). They are identical, of course, with the parameters of the corresponding mirror-antipodal pairs RR + RS and RR + SR. These parameters carry all the information on the influence of association on the n.m.r. spectra of binary mixtures of the diastereomers. In contrast to mixtures of enantiomers, the signals of epimers at equal concentrations naturally do not merge into one, and two signals are observed throughout the range of relative concentrations.

Table 6. Chemical shift of signals in $^{31}P-\{^1H\}$ n.m.r. spectrum of mixtures of epimers of (V) with c = 0.4 M in chloroform (I_{rel} is the relative integral intensity and $c_1 = [SS]/([SS]+[SR])$ or $c_1 = [SS]/([SS]+[RS])$

c_1	δ, ppm	I_{rel}	t, °C											
			–60	–50	–40	–30	–20	–10	0	10	20	30	40	50
							SS+SR							
0.7	δ_{SS}	0.7	0.33	0.22	0.14	0.09	0.05	0.03	0,02	0	0	0	0	0
	δ_{SR}	0.3	0.48	0.25	0.13	0.13	0.13	0.15	0.17	0.20	0.23	0,26	0,31	0.33
0.5	δ_{SS}	0.5	0.50	0.26	0.24	0.17	0.12	0.08	0.05	0.03	0	0	0	0
	δ_{SR}	0.5	0.54	0.30	0.18	0.16	0.17	0,20	0.26	0.26	0.30	0,32	0.35	0.39
0.3	δ_{SS}	0.3	0.61	0.45	0,35	0.27	0.17	0.13	0.09	0.06	0.03	0.01	0	0
	δ_{SR}	0.7	0.62	0.36	0.23	0.24	0.22	0.24	0.26	0.30	0.32	0.35	0,37	0;39
							SS+RS							
0.7	δ_{SS}	0.7	–0.22	–0.15	–0,09	–0.05	–0.04	–0,01	0	0	0	0	0	0
	δ_{RS}	0.3	0.70	0.42	0.30	0.25	0.24	0.26	0,27	0,29	0.32	0.35	0,38	0.41
0.5	δ_{SS}	0.5	–0.30	–0.22	–0.15	–0.08	–0.06	–0.04	0	0	0	0	0	0
	δ_{RS}	0.5	0.73	0.44	0.35	0.28	0.26	0.27	0,29	0,31	0.33	0,34	0,37	0.41
0.3	δ_{SS}	0.3	–0.36	–0.26	–0.18	–0.12	–0.08	–0.06	–0.03	0	0	0	0	0
	δ_{RS}	0,7	0.75	0.50	0.39	0.31	0.30	0.33	0.34	0.37	0,39	0,41	0.41	0,41

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*The reference signal adopted was δ SS at the given temperature.

Table 7. SCADA parameters for binary mixtures of epimers SS + SR and SS + RS of (V) in 0.4 M solution in chloroform at various temperatures.

t, °C	–60	–50	–40	–30	–20
δ_{SS}^{SR}	0.77	0,61	0,52	0,49	0.55
δ_{SS}^{RS}	–0.41	–0.31	–0.24	–0,16	–0.10
δ_{SR}^{RR}	0.69	0.39	0,27	0,21	0,19
δ_{SR}^{SS}	0.44	0,21	0,09	0,07	0.07
$\alpha_{SS}^{SR}/\alpha_{SS}^{SS}$	1.8	1,3	0,8	0,5	0.2
$\alpha_{SS}^{RS}/\alpha_{SS}^{SS}$	2.6	2.0	1,3	1,0	1,0
$\alpha_{SR}^{RR}/\alpha_{SR}^{SR}$	3.3	2,7	2,0	2,1	1.6
$\alpha_{SR}^{SS}/\alpha_{SR}^{SR}$	3.0	3.4	3,6	2,4	1.8

Figs. 6–9 contain theoretical curves representing the dependence of the parameters of the diastereomeric anisochronism spectrum for the mixtures of epimers SS + RS and SS + SR at various temperatures. Good agreement is evident between calculated and observed values.

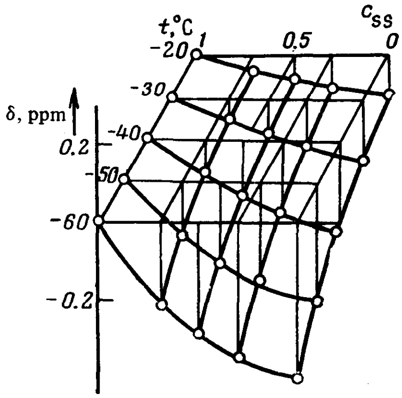


Figure 6. Dependence of chemical shifts in signals from SS isomer of (V) mixed with RS isomer in 0.4 M solution in chloroform on relative concentration at various temperatures. Each curve has been reckoned from the homoshift of the signal from SS molecules at the given temperature. The curves have been obtained theoretically, and the points represent experimental values.

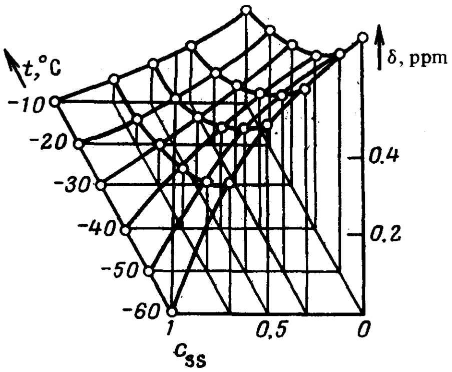


Figure 7. Dependence of chemical shifts in signals from SS isomer of (V) mixed with SR isomer in 0.4 M solution in chloroform on relative concentration at various temperatures. Each curve has been reckoned from the homoshift δSS at the given temperature. The curves have been obtained theoretically, and the points represent experimental values.

IV. DIASTEREOMERIC ANISOCHRONISM SPECTRA OF MORE COMPLICATED SYSTEMS

1. General Survey[19,20]

A general discussion of diastereomeric anisochronism spectra in terms of a plurality of theoretical ideas has shown[21] that the multiplicity of the spectra for mixtures of stereoisomers having n chiral fragments may equal the number of antipodal pairs 2^{n-1}, but cannot be less than or greater than this value. The multiplicity of such a spectrum of a mixture of stereoisomers may be increased if the asymmetrisation operators corresponding to the stereoisomers are non-degenerate and have mirror non-invariance. In achiral media with statistically controlled association, i.e. with rapid exchange between complexes, the multiplicity of the spectrum of a mixture of stereoisomers having n chiral centres may increase to 2^n, since under these conditions each stereoisomer has its own signal averaged over all association complexes of various compositions. If an achiral solvent contains a mixture of optical isomers containing N different components, the chemical shift of a nucleus in the ith component under SCADA conditions can be expressed by the formula

$$\delta_i = \left(\sum_{i=1}^{N} W_i^j \delta_i^j\right) \Big/ \sum_{j=1}^{N} W_i^j. \tag{17}$$

where δ_i^j is the chemical shift of a nucleus in the ith component in a primary interaction with the jth component and W_i^j is the statistical weight of the contribution to δ_i by this chemical shift, both parameters being averaged over all types of association complexes in which the ij interaction occurs, so that $\delta_i^j = \langle \delta_i^j \rangle$ and $W_i^j = \langle W_i^j \rangle$. As in the discussion of binary systems, it may be supposed that the statistical contribution of the interaction δ_i^j to δ_i is determined by the relative concentration

$$c_j = [j] \Big/ \sum_{j=1}^{N} [j]:$$

and the stability of the pair contacts α_i^j

$$W_i^j = \alpha_i^j c_j. \tag{18}$$

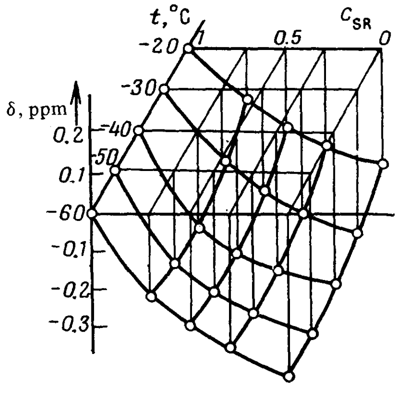


Figure 8. Dependence of chemical shifts in signals from SR isomer of (V) mixed with SS isomer in 0.4 M solution in chloroform on relative concentration of SR molecules at various temperatures. Each curve has been reckoned from the homo-shift δ_{SR} at the given temperature. The curves have been obtained theoretically, and the points represent experimental values.

Thus the chemical shift of the indicator nucleus in the ith component is given by

$$\delta_i = \left(\sum_{j=1}^{N} \alpha_i^j c_j \delta_i^j\right) \Big/ \sum_{j=1}^{N} \alpha_i^j c_j, \tag{19}$$

and the relative integral intensity of this signal by

$$I_i = [i] \Big/ \sum_{j=1}^{N} [j]. \tag{20}$$

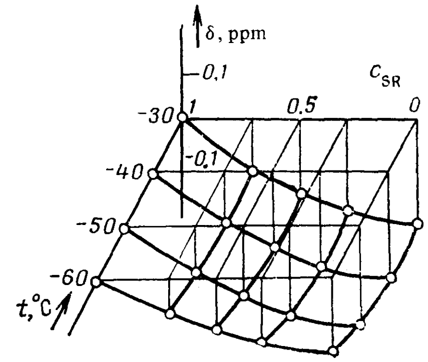


Figure 9. Dependence of chemical shifts in signals from SR isomer of (V) mixed with RR isomer [in 0.4 M solution in chloroform] on relative concentration at various temperatures. Each curve has been reckoned from the homo-shift δ_{SR} at the given temperature. The curves have been obtained theoretically, and the points represent experimental values.

The deduction of formulae (17) and (19) took into account the statistical contribution by pair contacts ij with rapid exchange between association complexes. More complicated contacts of the type ijq can in principle also be taken into consideration, when

$$\delta_i^j = \left(\sum_{q=1}^{N} W_{ij}^q \delta_{ij}^q\right) \Big/ \sum_{q=1}^{N} W_{ij}^q. \tag{21}$$

This formula covers long-range interactions, since components i and q are not in direct contact. Construction of a statistical theory for such systems of a second order of complexity gives rise to no fundamental difficulties, but the need for such complication can be ascertained only experimentally. It has been shown above that good agreement between calculated and observed chemical shifts of the diastereomeric anisochronism spectrum in binary systems is achieved with calculations based on formulae (15) and (16), or on Eqns. (7) and (8) for a mixture of enantiomers, in which only direct pair contacts are considered. We shall show below that a quaternary system can be completely analysed in terms of formula (19).

2. Four-component Systems[19,20]

For a mixture of four stereoisomers having two chiral centres we can apply Eqn. (19) to the chemical shift of phosphorus in each stereoisomer. With $N = 4$ the total number of α_i^j and δ_j^i parameters is 32, which are given in the two quadratic matrices

$$\begin{pmatrix} \alpha_{RR}^{RR}\alpha_{RR}^{SS}\alpha_{RR}^{RS}\alpha_{RR}^{SR} \\ \alpha_{SS}^{RR}\alpha_{SS}^{SS}\alpha_{SS}^{RS}\alpha_{SS}^{SR} \\ \alpha_{RS}^{RR}\alpha_{RS}^{SS}\alpha_{RS}^{RS}\alpha_{RS}^{SR} \\ \alpha_{SR}^{RR}\alpha_{SR}^{SS}\alpha_{SR}^{RS}\alpha_{SR}^{SR} \end{pmatrix} \quad \begin{pmatrix} \delta_{RR}^{RR}\delta_{RR}^{SS}\delta_{RR}^{RS}\delta_{RR}^{SR} \\ \delta_{SS}^{RR}\delta_{SS}^{SS}\delta_{SS}^{RS}\delta_{SS}^{SR} \\ \delta_{RS}^{RR}\delta_{RS}^{SS}\delta_{RS}^{RS}\delta_{RS}^{SR} \\ \delta_{SR}^{RR}\delta_{SR}^{SS}\delta_{SR}^{RS}\delta_{SR}^{SR} \end{pmatrix}$$

where the rows correspond to stereoisomers whose chemical shifts are under consideration (subscripts), and the columns to stereoisomers that interact with the former in elementary pair contacts. The right-hand matrix contains parameters describing the fields induced at the indicator nucleus in the association complexes, and the left-hand matrix parameters representing the stereospecificity of pair contacts in the complexes. With the use of these parameters formula (19) can be written for the chemical shift δ_i of each stereoisomer in the form

$$\delta_i = \frac{\alpha_i^{SS}c_{SS}\delta_i^{SS} + \alpha_i^{RR}c_{RR}\delta_i^{RR} + \alpha_i^{RS}c_{RS}\delta_i^{RS} + \alpha_i^{SR}c_{SR}\delta_i^{SR}}{\alpha_i^{SS}c_{SS} + \alpha_i^{RR}c_{RR} + \alpha_i^{RS}c_{RS} + \alpha_i^{SR}c_{SR}}, \quad (22)-(25)$$

in which the subscript i denotes respectively SS, RR, RS, and SR. When symmetry is taken into account, the number of independent parameters in these formulae is greatly diminished. Thus the parameters δ_i^j become equal when both partners in an interaction are replaced by mirror-image antipodes, and the number of such independent parameters decreases to 8. This applies also to the α_i^j parameters, but in this case we also have $\alpha_j^i = \alpha_i^j$, so that the number of these independent parameters diminishes to 6. Each set of 14 parameters corresponds, of course, to given selected conditions of the n.m.r. experiment (solvent, total concentration, temperature).

Table 8. Calculated chemical shifts of signals from stereoisomers SS and SR (or RR and RS) of (V) in a mixture of four isomers in 0.4 M solution in chloroform*.

t, °C	—60	—50	—40	—30	—20	—10	0	10	20	30	40	50
δ_{SS}	0.24	0,13	0.07	0.02	0	0	0	0	0	0	0	0
δ_{SR}	0,46	0,23	0.15	0.17	0.22	0.28	0.31	0.34	0.37	0.39	0.40	0.41
$\delta_{SR}—\delta_{SS}$	0.22	0,10	0.08	0.15	0.22	0.28	0.31	0.34	0 37	0 39	0.40	0.41
$\Delta\delta_{exp}$	0,19	0,09	0.08	0.17	0.24	0.29	0,31	0.34	0.37	0,38	0 39	0.41

*The homo-shift δ_{SS} at the given temperature was adopted as reference signal.

With an instrument of sufficiently high resolving power and with unequal relative concentrations of the four stereoisomers, the diastereomeric anisochronism spectrum should in general contain four signals with different chemical shifts δ_{SS}, δ_{RR}, δ_{RS}, and δ_{SR}. The relative intensities of the components of this quadruplet should be equal to the relative concentrations of the corresponding stereoisomers. If the stereoisomers are present in equal concentrations in the mixture, it is readily seen that the chemical shifts of the enantiomers RR and SS, and also of RS and SR, will become equal, their signals will coalesce, and the spectrum will contain two signals of equal intensity. This has been observed experimentally[20].

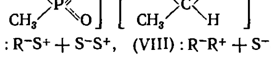
All the fourteen parameters required for the calculation had been determined earlier[20] in experiments on binary systems (Table 2 and 7). Values of $\delta_{SS} = \delta_{RR}$ and $\delta_{SR} = \delta_{RS}$ were calculated for various temperatures (Table 8). It is seen that $\Delta\delta$ actually passes through a minimum at −45°C, as illustrated by Fig. 2 (curve *V*). Agreement is observed between calculated and experimental values of $\Delta\delta$.

The molecules of quinine alkaloids contain four asymmetric carbon atoms, at positions 3, 4, 8, and 9. In natural (−)-dihydroquinine the centres at 3 and 4 have the (+) configuration, while 8 and 9 have the (−) configuration. The synthetic racemate, of course, has (±) at all centres. In general, therefore, a mixture of (−)-dihydroquinine and racemic dihydroquinine must be expected to exhibit a maximum of sixteen signals instead of the single signal of a given indicator nucleus. The fact that only two signals appear indicates that all centres of asymmetry other than one have little effect. It is most probably the chiral atom at position 9 that exerts this dominant effect.

3. Four-component Systems with Ion Exchange

An important part in experimental stereochemical investigations is played by the n.m.r. spectra of salts containing chiral cations and anions. Since Pasteur's time such salts have been used for resolving racemates. Their n.m.r. spectra have been widely applied during recent years to determine the optical purity of enantiomers, absolute configurations[9,29], etc. It is therefore important to know how the diastereomeric anisochronism spectrum of a mixture of enantiomeric or diastereomeric salts is formed, and to what extent the n.m.r. criterion is appropriate for solving the above problems.

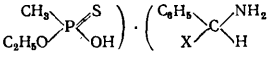
The dependence of the chemical shifts in the n.m.r. spectra of a mixture of the salts (VII) and (VIII)



(VII) : $R^-S^+ + S^-S^+$, (VIII) : $R^-R^+ + S^-S^+$.

on the enantiomeric composition was investigated by Mikolajczyk et al.[30] Here R and S denote the absolute configurations of the cations (R^+ and S^+) and the anions (R^- and S^-). The difference $\Delta\delta$ between the chemical shifts of the *P*-methyl protons were found to vary linearly with the relative concentration of the SS isomer over the range 27−78 mole % of one of the enantiomers.

Shipov et al. investigated[31] the $^{31}P-\{^1H\}$ n.m.r. spectra of salts (IX) of enantiomeric ethyl hydrogen phosphonothionates (R and S) with 1-phenylethylamine (R and S)



(IX) : X=CH_3; (X) : X=H.

at constant total concentrations 0.5 M and 1.0 M in a 1 : 1 mixture of chloroform and deuterochloroform between −50 and −10°C. The most detailed examination was made on a 0.5 M solution at −30°C. The enantiomeric salts RR and SS were prepared by the method of Boter and Platenburg[24], and the salts RS and SR by mixing the corresponding enantiomeric acids and anions. Their absolute configurations were established from data obtained by

Mikolajczyk et al.[29] The constants of the 1-phenylethylammonium and benzylammonium ethyl phosphonothionates investigated are listed in Table 9.

Table 9. Constants for stereoisomeric salts.

Absolute configuration	$[\alpha]_D^t$	t, °C
	(IX)	
RR	+10.00°	22
SS	−9.83°	22
RS	+5.33°	20
SR	−5.00°	20
	(X)	
R—	+7.83°	20
	—	—

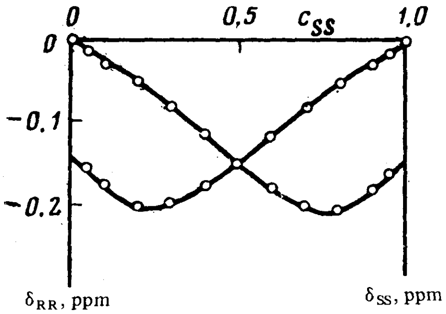


Figure 10. Dependence of δ_S and δ_R on relative content of antipodes of salt (IX) in 0.5 M solution in 1 : 1 $CHCl_3$–$CDCl_3$ at −30°C. The homo-shift δ_{SS} was adopted as reference signal.

Fig. 10 illustrates the experimental dependence of the ^{31}P n.m.r. chemical shifts of mixtures of the R^-R^+ and S^-S^+ enantiomers of the salt (IX) [20] at −30°C. A single signal is observed in the racemic mixture at −50°C, displaced by −0.27 ppm from the signal of the pure enantiomers (i.e. from the homo-shift). At all other concentrations two signals are observed. The curves differ markedly from the above cases of SCADA: they are butterfly-shaped with a minimum and an inflection, whereas typical SCADA curves with rapid exchange between association complexes do not (and cannot) contain either extrema or inflections. At −30°C the curves retain the "butterfly" character, but with narrower wings: i.e. the difference between the chemical shifts $\delta_R - \delta_S$ is smaller (Fig. 10).

Salt systems of this kind differ from the quaternary systems discussed in subsection 2 in the absence of a system of covalent bonds between the chiral centres in the stereoisomeric salts S^-S^+, R^-R^+, S^-R^+, and R^-S^+. In strongly dissociating media the chiral centres are kinetically independent; in media of low polarity they form ion-pairs or higher association complexes, between which, however, quite rapid ion exchange is possible [32].

In a solution of a mixture of the enantiomeric salts S^-S^+ and R^-R^+ in any relative concentrations, i.e. with $c^0_{SS} + c^0_{RR} = 1$, equilibrium is established between four ion-pairs:

$$S^-S^+ + R^-R^+ \overset{K}{\rightleftarrows} S^-R^+ + R^-S^+. \tag{26}$$

with the equilibrium constant

$$K = c_{SR}c_{RS}/c_{SS}c_{RR}, \tag{27}$$

where

$$c_{SR} = c_{RS};\quad c_{RR} + c_{RS} = c^0_{RR};\quad c_{SS} + c_{SR} = c^0_{SS}.$$

The chemical shifts in the n.m.r. spectra of such systems could apparently be considered in terms of additive contributions by $\delta_{R^-R^+}$ and $\delta_{R^-S^+}$ to δ_{R^-} and by $\delta_{S^-S^+}$ and $\delta_{S^-R^+}$ to δ_{S^-}. However, the $\delta - c$ relation obtained from theoretical curves calculated on the basis of this hypothesis does not resemble the experimental relation: curves for whose construction only ion exchange has been taken into account differ from the experimental curves in the absence of inflections and extrema at all values of c other than zero and unity. With salts of type (VII)–(IX) not only ion-pairs but also more complicated hydrogen-bonded complexes may be formed. The phosphonate anion is able to form only one hydrogen bond, and thereby fix an ion-pair, which therefore acts as an elementary particle in forming higher association complexes.

Thus in media of low dielectric constant the diastereomeric anisochronism spectra of stereoisomeric salts are produced under the influence of three factors—(*a*) formation of ion-pairs as stereoisomeric quasi-molecules, (*b*) ion exchange, i.e. the exchange of chiral centres between these quasi-molecules, and (*c*) association of the quasi-molecules—so that the problem of interpreting the spectra of such systems simplifies to the four-component problem of subsection 2 complicated by ion exchange [19,20]. The influence of these factors on the chemical shifts is expressed by the formulae

$$\delta_{R^-} \doteq (\Delta_{RR}c_{RR} + \Delta_{RS}c_{RS})/c^0_{RR}, \tag{28}$$

$$\delta_{S^-} = \Delta_{SS}c_{SS} + \Delta_{SR}c_{SR}/c^0_{SS}, \tag{29}$$

in which δ_{R^-} and δ_{S^-} are the chemical shifts of the indicator nucleus in R and S anions, while Δ_{RR}, Δ_{RS}, Δ_{SR}, and Δ_{SS} are those of the quasi-molecules R^-R^+, R^-S^+, S^-R^+, and S^-S^+ produced in conformity with SCADA principles, i.e. formulae (22)–(25). Thus a 33rd parameter—the equilibrium constant K—is added to the 32 parameters of a system comprising four two-centred stereoisomers given above as two quadratic matrices. In this case, too, allowance for symmetry reduces the number of δ_i^j parameters to 8, and of α_i^j to 6. The parameters δ^{SS}_{SS} and δ^{SR}_{SR} are determined directly in an experiment by measuring the chemical shift in solutions of the pure enantiomers RR (or SS) and SR (or RS).

The present problem requires knowledge of 13 independent parameters, to determine which we have used the pairs of diastereomeric salts $R^-R^+ + S^-R^+$ and $R^-R^+ + R^-S^+$. In an RR + SR mixture in solution no new species appear on ion exchange, and treatment of experimental data on the basis of formulae (28), (29), and (19) enables us to isolate the chemical-shift parameters

$$\delta^{RR}_{SR} = \delta^{SS}_{RS}\quad \delta^{SR}_{RR} = \delta^{RS}_{SS},$$

and also the constants

$$\alpha^{RR}_{SR} = \alpha^{SS}_{RS} = \alpha^{SR}_{RR} = \alpha^{RS}_{SS}.$$

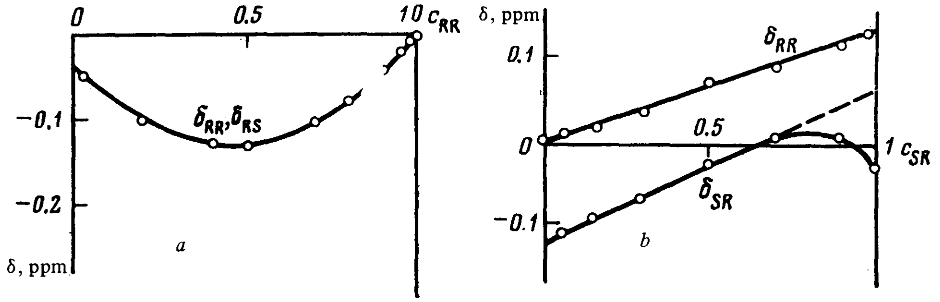


Figure 11. Dependence of chemical shifts of signals in spectra of binary salt systems (IX) on relative concentration: *a*) RR + RS; *b*) RR + SR.

If another pair of diastereomers—R^-R^+ and R^-S^+—is used, the parameters δ_{RS}^{RR} and δ_{RR}^{RS} and the equal δ_{SR}^{SS} and δ_{SS}^{SR}, as well as the parameters

$$\alpha_{RS}^{RR} = \alpha_{SR}^{SS} = \alpha_{RR}^{RS} = \alpha_{SS}^{SR}.$$

can be isolated similarly. Fig. 11 illustrates the experimental dependence of the chemical shifts of these pairs on their relative concentration†. Thus the number of unknown parameters can be reduced to two δ parameters (δ_{RR}^{SS} and δ_{RS}^{SR}) and two α parameters (α_{RR}^{SS} and α_{RS}^{SR}), together with *K*.

Comparison of theoretical and experimental δ(*c*) values with variation in the parameters α_{RR}^{SS} and α_{SR}^{RS} showed that these parameters could be taken as unity without any great error, so that the chemical shifts δ_{RR}^{SS} and δ_{RS}^{SR} and the constant *K* could be evaluated. The complete set of parameters of the system (with $K = 1.3$) is

$$\begin{array}{c} \alpha \\ \begin{array}{cccc} \mathrm{RR} & \mathrm{SS} & \mathrm{RS} & \mathrm{SR} \end{array} \\ \left(\begin{array}{cccc} 1.0 & (1.0) & 1.3 & 1.0 \\ (1.0) & 1.0 & 1.0 & 1.3 \\ 1.3 & 1.0 & 1.0 & (1.0) \\ 1.0 & 1.3 & (1.0) & 1.0 \end{array}\right) \end{array} \begin{array}{c} \\ \\ \mathrm{RR} \\ \mathrm{SS} \\ \mathrm{RS} \\ \mathrm{SR} \end{array} \begin{array}{c} \delta \\ \begin{array}{cccc} \mathrm{RR} & \mathrm{SS} & \mathrm{RS} & \mathrm{SR} \end{array} \\ \left(\begin{array}{cccc} 0 & -0.44 & -0{,}22 & +0.01 \\ -0.44 & 0 & +0{,}01 & -0{,}22 \\ -0.20 & -0{,}14 & -0.04 & -0.46 \\ -0.14 & -0{,}20 & -0{,}46 & -0.04 \end{array}\right) \end{array}$$

Fig. 10 shows the theoretical curve calculated with these values. Thus the chemical shifts observed in salt systems are due to the combined action of chemical equilibrium and SCADA. Consequently exclusion of the influence of the equilibrium factor should reveal pure SCADA. The ^{31}P n.m.r. spectra were investigated of salts of stereoisomeric R and S ethyl hydrogen phosphonothionates and benzylamine[20], in which system (X) the base is achiral. Hence the chemical shifts cannot be affected by ion exchange. In this case the experimental dependence of the chemical shifts on the relative concentration of the enantiomeric acid esters gives the usual SCADA curve with the parameters $\delta_h = 0$, $\delta_c = 0.25$, and $\alpha_c/\alpha_h = 2.4$.

The matrix elements α_i^j and δ_i^j (and *K* in the case of salt systems) carry the whole of the information on the influence of association on the n.m.r. spectra and its stereospecificity. It is better to use these parameters as physical characteristics of systems instead of the less informative quantity Δδ. The temperature variations of the matrix elements have interesting features, on whose basis we can discuss several physical aspects of the interaction of chiral molecules in the primary step of association.

The δ−*c* curves of binary systems have two parameters, $\delta_i^j - \delta_i^i$ and α_i^j/α_i^i, the first of which represents the range of variation in δ(*c*), and the second the departure of the curve from a straight line that occurs when $\alpha_c = \alpha_h$, i.e. in the absence of stereospecificity of interaction. Tables 2 and 7 show that for SS molecules the ratio $m_{SS}^j = \alpha_{SS}^j/\alpha_{SS}^{SS}$ decreases with rise in temperature. However, if in mixtures of SS with RR or with RS preference for one type of interaction is lost as the temperature rises (at the limit of disappearance of the observed effects stereospecificity is almost absent), in the SS + SR mixture interaction of SS with SR molecules becomes more preferred at low temperatures, a preference which is lost at −40°C, and with further rise in temperature homo-interaction of SS with identical SS molecules occurs in preference to interaction with SR molecules.

For SR molecules, depending on their partner in the mixture, rise in temperature may either increase (SR + SS) or lower the ratio m_{SR}^j. On the whole the great diversity of variation in *m* for different interactions indicates a non-linear variation in the energy of interaction of chiral molecules on intermolecular association depending on the interaction of individual elements of chirality. This conclusion is of fundamental importance.

The interpretation of the δ_i^j values and their temperature dependence (Tables 4 and 8) for each primary association complex is quite complicated. Without completely rejecting the influence of direct induction of additional magnetic fields at the indicator nucleus on diastereomeric anisochronism during association, nevertheless we must evidently assume that conformational changes are primarily responsible for its establishment and variation. The role of association in changing the position of the signal relative to a possible signal in an isolated molecule may consist in

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† Divergence from the statistical SCADA rules is observed on the δ_{SR} curve in the region of c_{SR} values close to unity (Fig. 11*b*), the reason for which is not yet clear. Perhaps an inadequate rate of exchange has an influence in this concentration range, and (or) more complicated association complexes play a more important part.

fixing a conformation with a different value of δ in the primary association complex. This applies, of course, not to a single act of pair association but to interactions between partners averaged over all types of association complexes. Furthermore, the fixation of conformations having a given values of δ implies, not a rigid set of particular conformations, but a redistribution of conformational populations. More detailed investigation of these mechanisms will evidently be possible only on the development of experimental and theoretical methods for quantitative analysis of nuclear shielding in complicated molecular structures.

An interesting series of papers published during 1975 to 1977 by French workers[33-37] reported a comprehensive investigation of the association of dipeptides of alanine, valine, and norvaline of general formula

$$R(1)-C(1)O(1)-N(2)H(2)-C_{\alpha}H_{\alpha}R(2)-C(2)O(2)-N(3)H(3)-R(3).$$

Infrared spectroscopy in tetrachloromethane solution revealed the presence of a conformational equilibrium between conformers A and B. In the former the hydrogen bond H(2)...O(2) completes a five-membered ring, but in conformer B the O(1)...H(3) bond closes a seven-membered ring. Conformer A has a strong intermolecular H(3)... O(1) hydrogen bond, but B is not characterised by association. The atom C_{α} is asymmetric.

Table 10.

R (2)	R (1), R (3)	$K'/2K$
CH_3	t-C_4H_9, iso-C_3H_7	0.9
C_3H_7	t-C_4H_9, iso-C_3H_7	3.3
iso-C_3H_7	t-C_4H_9, iso-C_3H_7	8.5

In full agreement with the results of Williams et al.[13], Horeau and Guette[1], and Soviet authors[15-20], these workers[33-37] observed a doubling of the multiplicity of signals in the n.m.r. spectra in non-equivalent mixtures of antipodes. The treatment that they used[33-37] in calculating Δδ for this specific problem was based on the same principles as the above general calculation of SCADA taking exchange into account. Their equations contain four δ parameters and eight x (concentration) parameters, which were determined from infrared and ^1H n.m.r. spectra. The results for stereoselectivity of association are given in Table 10, in which K' is the cross-dimerisation ($A^D + A^L$) constant, and K the homo-dimerisation ($A^D + A^D$ or $A^L + A^L$) constant. They show that the peptide of alanine is devoid of stereoselectivity of association, whereas those of norvaline and valine form dimers with a high degree of stereoselectivity.

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From the above considerations it is clear that SCADA, apparent in a higher multiplicity of n.m.r. spectral signals in a non-racemic mixture of optical antipodes, is a phenomenon that gives important information on association. When dissociating media (methanol, water) are used, or trifluoroacetic acid, which decomposes association complexes of chiral molecules, is added to non-polar solvents, increase in the multiplicity of n.m.r. spectra is not observed.

Investigation of intermolecular interactions of chiral molecules by other methods lies outside the scope of this Review. We will merely mention a series of studies by Wynberg et al.[38-40], in which the stereoselectivity of interaction of chiral molecules determined the reaction velocity and the proportions of products. Examples chosen were the oxidation of 5,6,7,8-tetrahydro-3,4,8-trimethyl-2-naphthyl ferricyanide, the reductive dimerisation of optically active and racemic camphor, and the reduction of camphor by lithium tetrahydroaluminate to borneol and isoborneol. Research on the spontaneous or seeded separation of racemates into antipodes is obviously of practical importance.

A prolonged "calm", during which solutions of antipodes were regarded in all cases as ideal, so that the possibility that the properties of one antipode would be affected by the presence of the other was thereby rejected *a priori*, has been followed by a period of thorough study of the stereoselectivity of interaction of antipodal molecules—a phenomenon which undoubtedly plays an important part in biological processes and in whose study the n.m.r. method is indispensable.

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Chemistry of Phosphinylidene Compounds—Advances and Prospects of Development

E.E.Nifant'ev

Research in this field is surveyed, and features of individual classes of compounds having this functional group in common are compared. An attempt is made to outline possible developments in certain promising scientific directions. Attention is paid mainly to investigations made during recent years. A list of 506 references is included.

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I. INTRODUCTION

The evolution of the chemistry of organophosphorus compounds has created a large region uniting many classes of compounds having a phosphinylidene functional group $OPH<$ in common. It comprises acids of tervalent phosphorus, their partial esters, thiolic esters, amides, certain anhydrides, etc., which can all be regarded as phosphinylidene derivatives. Their preparation, structure, reactions, and practical applications have now been widely investigated. Individual aspects of the results have been discussed in monographs and reviews. Thus Tsvetkov and Kabachnik published a comprehensive work[1] on the preparation and analysis of such derivatives. Other articles[2,3] were devoted to problems of alkylation. Individual classes of compounds—dialkyl phosphites[4,5], phosphonous acids and their derivatives[6], phosphinous acids[7]—have been subjects of compilations. The above reviews were written during the early and middle 1960s, and cover information that has become almost classical. Investigations made during recent years, which have been pursued especially vigorously, have not yet been summarised or examined from general points of view. The resulting need to fill the gap is intensified by certain circumstances, of which special note should be made.

1. The number of known classes and types of phosphinylidene derivatives has increased appreciably, which has permitted both comparison of the properties of a wide range of compounds having the same functional group and the first conclusions on the influence of structure of their reactivity. Moreover, it has become possible to pass from a qualitative to a quantitative treatment of the results.

2. A stereochemical principle has appeared. The first individual geometrical and optical isomers of partial phosphites, phosphonites, and phosphinous acids have been obtained. Research has begun on dynamic stereochemistry, in particular on the conformational dependence of the reactivity of phosphites.

3. Abundant preparative information has accumulated, and fundamentally new reactions of phosphinylidene compounds have been suggested. The widespread uses of several transformations discovered during the 1940-1950s has made it necessary to honour the debt to their authors and introduce the appropriate names into chemical vocabulary.

4. Physicochemical laboratories have been attracted to the study of phosphinylidene compounds. It is significant that not only structural and kinetic but also preparative problems have been solved in them, revealing unexpected possibilities for organophosphorus synthesis.

5. Methods used in the chemistry of phosphinylidene compounds have been applied to naturally occurring compounds and polymers. Original results have been obtained, indicating a promising future for these lines of investigation.

6. Work on the technology of dialkyl phosphites and related derivatives has ended in industrial realisation. Data have been obtained on the use of phosphinylidene derivatives to solve many practical problems.

The present Review has been prepared in the light of the above circumstances. It reflects (but does not always fully cite) the advances of the past decade. The Reviewer has seen his task in not only systematising and analysing published information but also assessing tendencies and the prospects for development of the most interesting lines of research. Judgments on such problems are, of course, controversial in character.

II. SYNTHESIS

Published information usually covers the preparation of phosphorous diesters, multisubstituted phosphonous esters, and oxides of secondary phosphines. During recent years, however, other related types of compounds have become accessible, including relatively unstable derivatives; in several cases stereoisomeric forms have been isolated and studied.

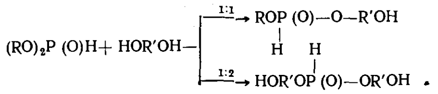
In the present Section information on the formation of phosphinylidene compounds is presented in a sequence based on chemical structure—(1) organic derivatives of phosphorous acid, (2) phosphonous acids and their derivatives, (3) phosphinous acid, (4) derivatives of hypophosphorous acid, and (5) oxides of primary phosphines and other compounds—where preparations of each class or type of compounds are separated into two groups: the first group comprises reactions in which the initial substances already contain a phosphinylidene function, and the second those in which it is formed. Where possible, data on the structure of stereoisomers are included.

1. Organic Derivatives of Phosphorous Acid

(*a*) Diesters

Dialkyl (diaryl) phosphites. The most thoroughly studied and important type of phosphinylidene derivatives comprises dialkyl and diaryl phosphites. They are widely used as intermediates in the production of pesticides[8] and complexing agents[9,10], as stabilisers for polymers[11,12], additives to oils[13,14], components of flame-proofing compositions[15], etc.

To prepare many dialkyl (diaryl) phosphites it is advisable to phosphinylate alcohols (phenols) with simple derivatives. This includes transesterification, whose advantages include high yields and mild conditions due to the absence of aggressive by-products, as well as simplicity of control. Transesterification has been used to prepare various symmetrical and unsymmetrical phosphites[16-18], phosphinylated terpenes[14], and polyfunctional systems, mainly hydroxylated phosphorous esters formed from simple dialkyl phosphites and glycols[19-21]

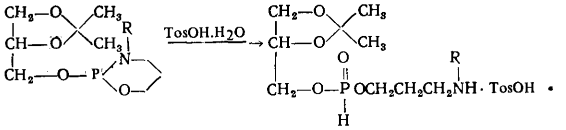


$$(RO)_2P(O)H + HOR'OH \begin{cases} \xrightarrow{1:1} ROP(O){-}O{-}R'OH \\ \qquad\quad\;\; | \\ \qquad\quad\;\; H \\ \qquad\qquad\qquad\; H \\ \qquad\qquad\qquad\; | \\ \xrightarrow{1:2} HOR'OP(O){-}OR'OH \end{cases} .$$

The products are phosphites of a new type, of interest for macromolecular chemistry. Their preparation by other routes is complicated or altogether impossible. However, transesterification has its limitations. Thus negative results have been obtained in the phosphinylation of 2-trichloromethylpropan-2-ol with simple dialkyl phosphites[22]. Because of such difficulties attention has been attracted to the alcoholysis of amides[23-25] and thiolic esters[26] of phosphorous acid, as well as the corresponding mixed anhydrides[27], which are milder reagents.

It has been proposed to obtain dialkyl phosphites of diverse structure by esterifying phosphorous acid[28,29], which is of industrial interest[30]. Similarly, monoalkyl phosphites can also be esterified[31,32]; those of more complicated structure, e.g. nucleoside phosphites, are esterified in the presence of condensing agents[33]. Phosphorous acid and monoalkyl phosphites can be alkylated to dialkyl phosphites by means of diazo-compounds[34,35], orthoesters[36], oxiran[37], and alkyl halides[38].

A large group of reactions yielding dialkyl or diaryl phosphites is based on the use of three-coordinated phosphorous derivatives. An important approach is hydrolysis of $(RO)_2PX$ systems, where X = Cl,[22,39] OAlk[†],[40-42] or NH_2.[43-45] The hydrolysis of complex phosphoramidites requires meticulous selection of conditions; thus treatment of the cyclic 2,3-isopropylideneglycerol phosphoramidite with water gives a mixture of products, but with the hydrate of toluene-*p*-sulphonic acid the required compound is formed in almost quantitative yield[44]:



In some cases a phosphorus-carbon bond may be cleaved. An example is the hydrolysis of completely esterified carborane-phosphonites[46]:

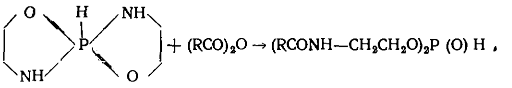
$$RCB_{10}H_{10}CP(OC_2H_5)_2 + H_2O \rightarrow (C_2H_5O)_2P(O)H + RCB_{10}H_{10}CH .$$

The preparation of acid phosphites by decomposing the neutral esters is especially valuable. Some esters, primarily those of tertiary alcohols, are degraded thermally[47]. More often, however, decomposition is effected by the use of acids—phosphorous acid[48] or dialkyl phosphorodithioates[49]— of which the latter ensure the highest rates because of the strongly nucleophilic character of the anion. An especially popular method is to dealkylate neutral phosphites with hydrogen chloride: for example[16]

$$CH_3OPCl_2 + 2C_6H_5OH \rightarrow [CH_3OP(OC_6H_5)_2 + HCl] \rightarrow (C_6H_5O)_2P(O)H + CH_3Cl .$$

A similar dealkylation completes a series of processes in the industrial production of dialkyl phosphites from phosphorus trichloride and alcohols. A continuous scheme has been suggested[50] for the process.

Much attention has been paid to the preparation of dialkyl phosphites from phosphorus sesquioxide and other anhydride systems. Direct alcoholysis of the oxide, a promising starting material for organophosphorus synthesis, leads to its complete conversion into an equimolecular mixture of mono- and di-alkyl phosphites[51]. If the reaction is conducted in boiling xylene, i.e. under conditions of azeotropic removal of water, monoalkyl phosphites are completely converted into the dialkyl esters, and a single product is formed[52]. When the technical "alcoholysate" is heated, monoalkyl phosphites disproportionate into the dialkyl esters and phosphorous acid[53]. It has been proposed to obtain dialkyl phosphites also by alcoholysis of anhydrides of alkyl dihydrogen phosphites[54,55] and by the deacylation of acyl phosphites[56,57]. An autodeacylation stage is probably involved also in passing from diaminospirophosphoran to bisacylaminoethyl phosphites[58]:



$$+ (RCO)_2O \rightarrow (RCONH{-}CH_2CH_2O)_2P(O)H ,$$

A special case of the formation of phosphorous diesters is the hydrolysis of α-oxo-phosphonates[59] and their imines[60]. It has been little studied, but is promising for the industrial production of dialkyl phosphites from white phosphorus, alcohol, and oxygen[61].

Alkylene (arylene) phosphites. Cyclic acid phosphites were first mentioned at the beginning of the century, but subsequently their study began only during recent years, when it has become possible to synthesise symmetrical and unsymmetrical 5–8-membered systems derived from glycols, dihydric phenols, and higher polyols. The most detailed investigation has been made on 1,3,2-dioxaphosphans—esters of 1,3-diols—which are of chemical and stereochemical interest, and structurally similar to certain bioregulators[62].

Simple and functionally substituted derivatives are usually obtained by transesterification[63-66]. Another popular approach involves modifying cyclic derivatives containing a three-coordinated phosphorus atom, by the hydrolysis of phosphorochloridites[67-71] and neutral mono- and bicyclo-phosphites[42,72], the acidolysis of phosphoramidites[63,64,66,73], or the aminolysis of pyrophosphites[74]. In several cases it is advisable to effect the preparations via thermally labile t-butyl intermediates[47,75,76].

Stereochemical factors must be taken into account in preparing substituted alkylene phosphites, owing to the possible formation of geometric isomers. A significant advance has been the development of directed methods for obtaining isomers. For example, 1-methyltrimethylene

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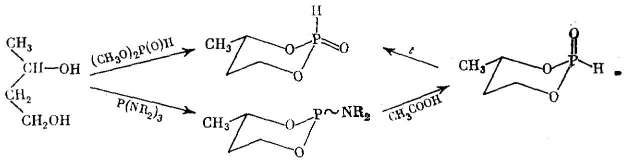
[†] A reaction mechanism differing from the traditional mechanism is discussed in Ref. 42.

phosphite is formed mainly as the *cis*-isomer when obtained by transesterification, but as the *trans*-isomer when obtained by the acidolysis of 1-methyltrimethylene phosphoramidites; the latter isomer is unstable, and changes its configuration when heated[63];

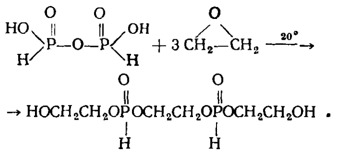


The orientation of the phosphinyl group and other structural factors in these rings have been investigated by proton nuclear magnetic resonance[63,64,66,68,69,77,78], dipole moments[63,77], infrared spectroscopy[69,79], and X-ray diffraction[80]. Moreover, several aspects of the dynamics of trimethylene phosphites—conversion of labile into stable geometric isomers[42,69,81], conformational equilibrium of symmetrical forms[79,82]—have been studied quantitatively. Geometric isomers of ethylenic phosphites do not exhibit ready interconversion[70]. Thus an appreciable difference exists between five- and six-membered cyclic phosphinylidene derivatives.

Alkylene diphosphites. These compounds, whose investigation has only just begun, have been obtained by transesterification[83]:

$$2\,(RO)_2P\,(O)\,H + HOR'OH \rightarrow RO{-}P\,(O)\,(H){-}OR'O{-}P\,(O)\,(H){-}OR\ ,$$

Opportunities for their technical use have been shown[84,85]. An unusual reaction giving an important product utilises pyrophosphorous acid and oxiran[86]:

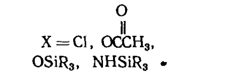


Poly(alkylene phosphites) and phosphites of polyhydroxylated polymers. It has been proposed[87-90] to obtain oligomeric and polymeric acid phosphites by the interaction of equimolecular quantities of simple dialkyl phosphites and glycols. The process develops differently according to the size of the alkylene radical: either a polyester is produced immediately or an initially formed alkylene phosphite polymerises. Unfortunately, many aspects of this promising reaction have not yet been elucidated.

A particular but important method for obtaining these polyesters is thermolysis of bis-2-chloroethyl phosphite. It is assumed that initial cyclisation to ethylene phosphite is followed by its condensation[91,92]. Polytransesterification has been extended also to triols, tetraols, and hexitols[93,94]. Several polyphosphites of hexitols have been suggested for use as additives to transformer oils[94].

Macromolecular acid phosphites of a different type are obtained by treating hydroxylated polymers with simple phosphinyl compounds. It is significant that these phosphinylating agents are more reactive than corresponding derivatives of quinquevalent phosphorus [Sic.] They have special advantages over various chlorides that are popular phosphinylating agents for lower alcohols and polyols, for their use does not liberate hydrogen chloride, which degrades or modifies many polymers. The phosphinylation of cellulose has been investigated in the greatest detail, for which purpose dialkyl phosphites[95-97], monoalkyl phosphites[96,97], and phosphorous acid[97] have been proposed. Polyphosphites, like other products of polymer-analogous reactions, are not chemically homogeneous. Amylopectin[98], lignin[99], polyallyl[100] and polyvinyl[101] alcohols, and soluble phenol–formaldehyde resins[102] undergo phosphinylation similarly to cellulose.

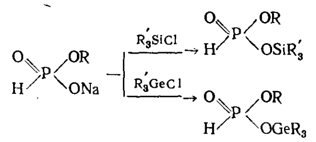
Trialkylsilyl phosphites. Silyl phosphites are definite analogues of the alkyl esters. They are usually obtained by the action of various silylating agents on phosphorous acid[103-106]:



$$(HO)_2\,P\,(O)\,H + 2R_3SiX \rightarrow (R_3SiO)_2P\,(O)\,H$$
$$X = Cl,\ O\overset{\overset{\displaystyle O}{\|}}{C}CH_3,\ OSiR_3,\ NHSiR_3\ .$$

Excess of the agent is not advisable, since neutral silyl phosphites might be formed. An interesting variant of this reaction, convenient for preparative purposes, is the interaction of phosphorous acid and a trialkylsilane in the presence of colloidal nickel[107]. Disilyl phosphites can be obtained by the alcoholysis or silanolysis of trisilyl phosphites[108], and also by the oxidation of disilyl hypophosphites[109].

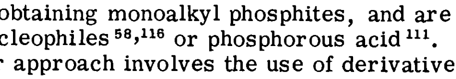
Alkyl silyl phosphites are formed by the reaction of monoalkyl phosphites with hexa-alkyldisiloxanes[110] and with trialkylchlorosilanes[105]; germanium derivatives are obtained similarly[105]:



(*b*) Monoesters

Phosphorous monoesters have been known for a long time, but their active investigation began only during recent years, probably stimulated by the discovery of interesting opportunities for their bio-organic use, as well as in solving practical problems[111]. As the first and second hydroxy-groups in phosphorous acid are esterified at different rates, a simple and convenient method has been developed for obtaining monoalkyl phosphites[28]. Phosphorous acid is poorly esterified by phenols, in contrast to alcohols[112]. The presence of a condensing agent—a carbodi-imide[113] or a sulphonyl chloride[113]—is advisable for the phosphinylation of complicated compounds (e.g. nucleosides). Phosphorous acid can be converted into monoalkyl esters by heating with alkyl halides[38] or t-butyl esters[114].

Other methods are transesterification[31,96] and the addition of hypophosphorous acid to quinones[115]:



Appropriate diesters are often used as initial compounds in obtaining monoalkyl phosphites, and are dealkylated by nucleophiles[58,116] or phosphorous acid[111].

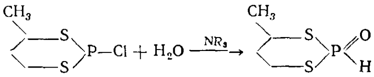
Another approach involves the use of derivatives of three-coordinated phosphorus. Thus it has been suggested that Menshutkin acid chlorides, including nucleosides, should be hydrolysed[117-119] or treated with t-butyl alcohol[120,121]. Hydrolysis has been applied also to neutral phosphites [122], phosphorodiamidites[123], and the corresponding spirophosphorans[124].

(*c*) Thiolic esters

Compounds of the type $OPH(SR)_2$ and $OPH(SR).OR$ began to be investigated only during the 1970s, when a fundamental difference from other phosphinylidene derivatives immediately became apparent. An attempt to prepare dithiolic esters by the thiolysis of tetra-alkyl phosphorodiamidites was reported; the products were neutral trithiolic esters, formed by disproportionation of the dithiolic esters [24,125]:

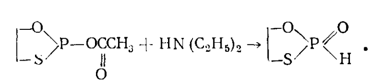
$$(R_2N)_2P(O)H + 2R'SH \rightarrow [(R'S)_2P(O)H] \rightarrow (R'S)_3P\ .$$

The required compounds are formed by the hydrolysis of dialkyl phosphorochloridodithiolites [26,125]. The clearest results are obtained with dithiols giving cyclic products[125]:



Cyclic chloridodithiolites are converted into phosphinylidene derivatives also by treatment with t-butyl alcohol[126]. Diethyl phosphorodithiolite is assumed to be formed in the hydrolysis of triethyl phosphorotrithiolite [127].

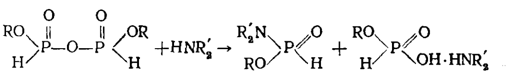
Only one phosphoromonothiolite—the ethylene ester—has been investigated. It has been prepared by hydrolysis of the corresponding chloride [128] and similar reactions, e.g. [128,129]



(*d*) Amides

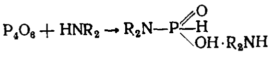
Phosphinylidene compounds containing a phosphoramide bond are of very great chemical interest. Various derivatives of this class—$OPH(NR_2)_2$, $OHP(NR_2).OR'$, $OHP(NR_2).OH$—are now known. Many diamides of phosphorous acid can be obtained by transamidation [24]. However, simple derivatives are mostly prepared by hydrolysis [130] or acidolysis [130,131] of fully amidated phosphorous acid. The required compounds can be obtained from triamides and propiolactone [132], and also from silyl phosphorodiamidites and alcohols[133]. It has been suggested that cyclic amides can be obtained by hydrolysing appropriate acid chlorides [66] or by treating them with t-butyl alcohol [134]. Data have appeared on the stereochemistry of these rings [135]. Salts of phosphorodiamidous acids are formed by reducing complete amides of phosphoric acid with alkali metals [136].

Phosphoramidous esters have been obtained by transamidation of simpler compounds [23], partial alcoholysis of diamides [24], and aminolysis of anhydrides containing a phosphinylidene group [137]: for example



Another method is hydrolysis of phosphoramidochloridous [137,139] or phosphorodiamidous [23,138,139] esters, as well as alcoholysis of anhydrides of phosphoramidous acids [54].

Monoamides of phosphorous acid have been described in only one patent [140]:



$$P_4O_6 + HNR_2 \rightarrow R_2N{-}P\begin{matrix}{=}O\\ {-}H\\ {-}OH\cdot R_2NH\end{matrix}\ .$$

(*e*) Acid halides

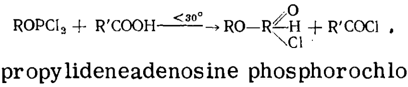
Results on the preparation of acid halides of phosphorous acid, containing a phosphinylidene group, have not yet been analysed in reviews on the phosphorus chemistry. It has evidently been assumed that these compounds are too unstable to exist. Nevertheless, such acid halides have been obtained.

Attempts have been made to prepare phosphorodichloridous acid by the action of hydrogen chloride on diamides of phosphorous acid, but the product isolated was phosphorus trichloride. The initial substance had obviously disproportionated under the reaction conditions, like other phosphinylidene compounds containing electron-accepting groups [24]:

$$(R_2N)_2P(O)H + HCl \rightarrow [Cl_2P(O)H] \rightarrow PCl_3\ .$$

Another route to an acid dichloride consists in treating phosphorus trichloride with diethyl phosphite: formation of a product was detected by n.m.r. at −40°C. [141]

A very interesting result has recently been obtained [142]:



$$ROPCl_2 + R'COOH \xrightarrow{<30^\circ} RO{-}R\begin{matrix}{=}O\\ {-}H\\ {-}Cl\end{matrix} + R'COCl\ .$$

2′, 3′-Isopropylideneadenosine phosphorochloridite has been prepared by selective hydrolysis of the corresponding Menshutkin acid chloride. The product was then oxidised and hydrolysed to 2′, 3′-isopropylideneadenylic acid [119].

Phosphorodifluoridous acid is obtained by redox reactions [143,144] and cleavage of its anhydrides by nucleophilic compounds [145,146]: for example

$$F_2PH + H_2O \rightarrow F_2P(O)H + H_2\ ,$$

$$F_2P(O)N(CH_3)_2 + 3HI \rightarrow F_2P(O)H + (CH_3)_2\overset{\oplus}{N}H_2\overset{\ominus}{I} + I_2\ .$$

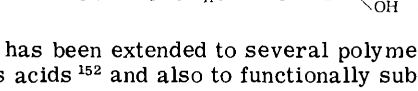
The product could be distilled (b.p. 67.7°C) and its structure proved. It disproportionates on storage [145,146]. Phosphoromonofluoridous acid and its deuteriated derivatives have been obtained by treating phosphorus trichloride with aqueous hydrofluoric acid [147]. It is easily converted into stable salts. Its methyl ester has been prepared by the reaction [146]

$$F_2P(O)H + F_2POCH_3 \rightarrow PF_3 + CH_3OP(O)FH\ .$$

2. Phosphonous Acids and their Derivatives

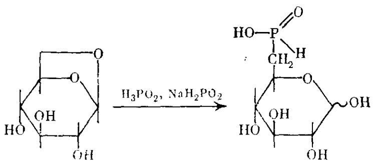
(*a*) Phosphonous acids

Phosphonous acids have been little studied as a class of compounds, but are of chemical interest and show promise for practical application. Alkylphosphonous acids are best obtained by the radical phosphinylidenation of alkenes [148-151]:



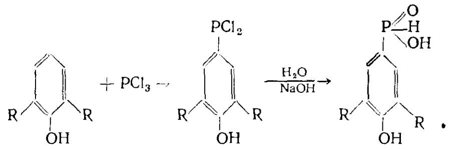
$$RCH{=}CH_2 + NaH_2PO_3 \xrightarrow[H^{\oplus}]{RO\cdot} RCH_2{-}CH_2{-}P\begin{matrix}{=}O\\ {-}H\\ {-}OH\end{matrix}$$

The method has been extended to several polymeric phosphonous acids [152] and also to functionally substituted systems[153,154]. The phosphinylidenation of hetero-unsaturated compounds—Schiff bases[155,156], hydrazones[157], oximes[158], etc.—has been studied. Certain anhydroaldopyranoses (e.g. levoglucosan) on reaction with hypophosphorous acid give 6-deoxy-6-glycophosphonous acids[153]:



The process probably involves formation and rearrangement of the hypophosphite, like the reaction of polyallyl alcohol with hypophophorous acid[159].

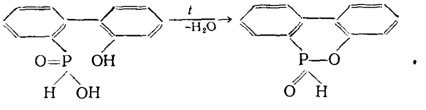
Alkyl- and aryl-phosphonous acids are often obtained by hydrolysis of their acid chlorides and other derivatives[6]. When especially pure products are required, hydrolysis must be replaced by treatment with t-butyl alcohol[160]. Acid dichlorides may yield fairly unusual acids: an example is the reaction[161]



Individual phosphonous acids are formed by the oxidation or the disproportionation of oxides of primary phosphines[162].

(*b*) Phosphonous monoesters

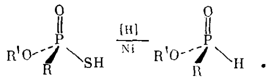
Acid phosphonites have been obtained by esterifying phosphonous acids with alcohols[28] and polyols[150,163,164]. In the latter case primary hydroxy-groups are phosphinylated preferentially. Esterification of phosphonous acids by phenols has not been reported. This reaction may well be possible under certain conditions, in view of the transformation[165-167]



For preparative purposes it is often more convenient to phosphinylate by transesterification. This process has been widely used with diols[168-170], tri- and tetra-ols,[83] carbohydrates[171], and cellulose[95].

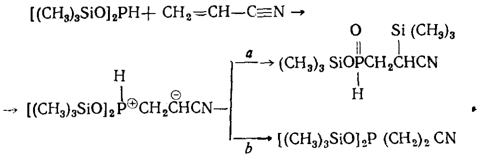
Another route starts from three-coordinated phosphorus derivatives, most frequently acid dichlorides, whose alcoholysis in the presence of amines has become widely used[172-174]. Sometimes it is convenient to treat dichlorophosphines with an equimolecular quantity of the alcohol (phenol) and t-butyl alcohol[175,176]. Acid phosphonites are formed also by the alcoholysis of phosphonous anhydrides[54,55], and the hydrolysis and acidolysis of neutral phosphonites[1] and phosphonoamidites[123,171].

In contrast to most classes of phosphinylidene compounds, acid phosphonites are often obtained from phosphorus(V) derivatives, for which purpose degradative reactions—hydrolysis of phosphonimidates[60], photochemical alcoholysis of phospholen oxides[177,178]—can be used. A very original method is the reduction of acid phosphonothioates with hydrogen over Raney nickel. This reaction can be used for the stereoselective formation of optically active compounds[179]:



Deselenation of phosphonoselenoates occurs similarly[180,181]. Optically active phosphonites can be obtained by stereospecific inclusion on cyclodextrans[182].

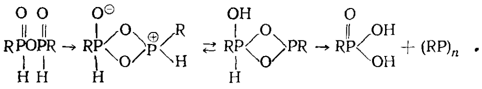
It has been proposed to obtain silicon[105,106,183], germanium[105], and antimony[184] analogues of acid phosphonites from the phosphonous acids and the corresponding hetero-organic halides. More complicated compounds of this type with additional functional groups are formed from disilyl hypophosphites and carbonyl compounds[185,186] or acrylonitrile[187]. The latter reaction apparently begins with formation of an adduct, which can then be transferred in two ways—(*a*) and (*b*):



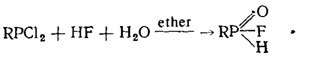
At low temperatures the rates of reactions (*a*) and (*b*) are comparable; at high temperatures $k_a > k_b$.

(*c*) Monoamides and monohalides of phosphonous acids

These compounds have been very little studied. The monoamides can be obtained by partial hydrolysis[171] or by acidolysis[131] of the full amides. The latter reaction is usually complicated by anhydridisation[131]; the resulting anhydride is unstable and disproportionates:

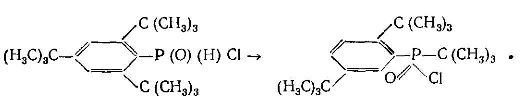


Phosphonous monofluorides have recently been obtained by a very simple process[188]:



$$RPCl_2 + HF + H_2O \xrightarrow{\text{ether}} RP(O)(F)H \ .$$

These compounds distil without decomposition. The corresponding chlorides are formed by acidolysis of alkyldichlorophosphines[189,190]. They are unstable and are readily dehydrochlorinated, which again emphasises the difference between chlorides and fluorides of phosphorus. 2,4,6-Tri-t-butylphenylphosphonochloridous acid exhibits its instability by isomerising[191]:



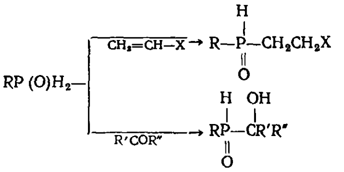
3. Phosphinous Acids

In laboratory practice it is convenient to obtain dialkyl- and diaryl-phosphinous acids from simple dialkyl phosphites and Grignard reagents[1,192,193]:

$$(C_2H_5O)_2P(O)H + 3RMgX \rightarrow R_2P\text{—}OMgX \xrightarrow{H_2O} R_2P(O)H \ .$$

Unsymmetrical phosphinous acids are formed from acid phosphonites by an analogous scheme. A stereochemically directed preparation could be achieved by using optically active phosphonites[194].

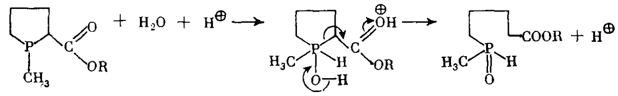
Buckler and Epstein[162] made a series of syntheses from oxides of primary phosphines together with alkenes, which might be functionally substituted, and also carbonyl compounds:



X=CN, C(O)NH$_2$.

The latter reaction has recently been extended to the preparation of phosphinous acids of the phosphan series[195].

Much research has been devoted to obtaining phosphinous acids from compounds already containing the essential molecular skeleton. Thus dimethylphosphinothious acid is hydrolysed by alkali to dimethylphosphinous acid[196]. This hydrolysis is unusual: the phosphinothioyl group in sulphides of tertiary phosphines is not converted into phosphinyl under similar conditions[196]. Thorough studies have been made of the hydrolysis of acid chlorides[60,161,197-199], anhydrides[200], esters[197,201], and amides[197] and of the thermolysis of t-butyl phosphinites[202]. The oxidation of secondary phosphines has been investigated in detail[203,204]. We can include here the acid hydrolysis of a cyclic phosphine[205]:



Other studies have been made on the preparation of phosphinous acids from phosphorus(V) derivatives. Reduction of phosphinous esters with lithium tetrahydroaluminate[194] and the desulphurisation (deselenisation) of phosphinothious (phosphinoselenous) acids with Raney nickel have been suggested; Michalski has obtained optically active products by using optically active acids[206]. Reducing processes applied to oxides of tertiary phosphines may be accompanied by rupture of a phosphorus-carbon bond[207]. α-Substituted phosphine oxides are degraded especially readily[60,208]. It is interesting that the phosphorus atom retains its configuration during their decomposition[208].

Unsymmetrical phosphinous acids have quite recently been used for fine structural investigation. Thus phenyl-s-butylphosphinous acid, which contains chiral carbon and phosphorus atoms, has been studied by n.m.r., which detected the presence of two pairs of diastereomers[209].

4. Hypophosphorous Esters and Oxides of Primary Phosphines (Phosphinyl Compounds)

Alkalyl hypophosphites were first obtained by Kabachnik et al.[210] by treating hypophosphorous acid with diazoalkanes:

$$H_2P(O)OH + RCHN_2 \rightarrow H_2P(O)OCH_2R \ .$$

These compounds have been obtained also by the action of hypophosphorous acids on orthocarbonyl compounds[211,212], neutral phosphites[213], and alcohols[214-216]. This last reaction was extended to diols[214,217] and hydroxylated polymers[101,218]. It has been shown recently that acid hypophosphites can be obtained by hydrolysis of the neutral compounds[219]. Hypophosphites, especially simple members of this group, are extremely labile and change when kept for a short time[210,213,219], but they can be stabilised by alcohols[214,219].

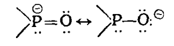
Monosilyl hypophosphites have been obtained by alcoholysis of the disilyl compounds and by silylation of ammonium hypophosphite with trialkylchlorosilanes[108]. Oxides of secondary phosphines can be obtained by oxidising primary phosphines with hydrogen peroxide, and also by the action of phosphine itself on carbonyl compounds[162]:

$$PH_3 + RCOR' \rightarrow [RR'C(OH)PH_2] \rightarrow RR'CHP(O)H_2 \ .$$

III. CHEMICAL REACTIONS

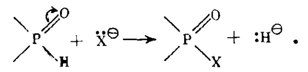
The phosphinylidene group provides a clear example of a functional group having a high and diverse reactivity. These compounds have therefore become key reagents in organophosphorus synthesis and important subjects for research on theoretical aspects of reactivity. Yet the character and the scale of development of the chemistry of phosphinylidene compounds have created the problem of a rational classification of their reactions, which are numerous and of diverse kinds. Evidently this could be most usefully based on the electronic factors determining the primary reaction step. We can then distinguish the processes indicated below.

1. Acid-base equilibria and salt formation. Here we include dyadic protropy.
2. Electrophilic reactions involving an ambident anion

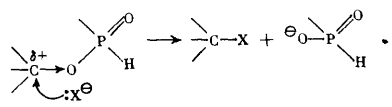


or the tautomeric form >P̈–OH.

3. Nucleophilic reactions occurring at the phosphorus atom bearing a partial positive charge:



Dialkyl phosphites and similar ester systems possess another centre, more open to attack by an anion:



4. Radical reactions resulting from homolysis of a phosphorus-hydrogen bond.
5. Phosphinylation, consisting in the introduction of a phosphinylidene group into the molecule of a nucleophilic compound and accompanied by loss of an anionoid group from the phosphorus. Incorporation of an amphoteric reagent at the X-P bond may be a particular case of such phosphinylation.

Unfortunately, it is not yet possible to use this scheme as a basis for the systematic arrangement of published information, since the mechanisms of many reactions have been little investigated or are altogether obscure. Furthermore, there is a large group of transformations whose initial stages are evidently related but whose subsequent stages are so different that they ultimately yield products of diverse chemical nature. Such conditions obviously justify use of a system based primarily on the mechanisms of the reactions undergone by phosphinylidene compounds but also allowing for the structure of the reaction products and other chemical circumstances. A convenient form of such an approach will be to divide the reactions into the five groups below.

1. Acid–base interactions, including tautomerism, salt formation, and complex formation.
2. Replacement of the hydrogen atom in the phosphinylidene group by a hydrocarbon radical or group.
3. Reactions not involving the phosphinylidene functional group.
4. Reactions accompanied by a decrease in the coordination number of the phosphorus atom.
5. Other reactions of phosphinylidene compounds.

This scheme does not include many widely used reactions, consisting in the replacement of groups attached to the phosphinylidene group, e.g. alcoholysis of esters, thioesters, and amides and the action of Grignard reagents on dialkyl phosphites. We have already discussed such processes in Section II, as methods for passing from one phosphinylidene compound to another.

1. Acid–Base Interactions, Salt Formation and Complex Formation

(*a*) Phosphinylidene compounds as acids and bases

Little experimental research has been done on the acidity of phosphinylidene compounds. Grayson[192] used potentiometric titration to study several arylphosphinous acids, under conditions that were not comparable for different specimens. Hammond[220] assessed the acidity of diethyl phosphite in water from results on isotope exchange‡. Moedritzer[221] showed by n.m.r. that the acidities of dibutyl phosphite and ethanol in diglyme were closely similar. These studies made in the early 1960s did not attract attention because of the disconnected and fragmentary character of the results. Systematic investigation was probably hindered by experimental difficulties and the low acidity of the compounds.

Kabachnik et al.[222] have just made a fundamental study of the acidity of dialkyl phosphites, alkyl phosphonites, and phosphinous acids by the use of transmetallation in dimethyl sulphoxide. The dissociation constants of these derivatives increase significantly in the above sequence. This work[222] is distinguished by rigorous assessment of the experimental characteristics of the proposed method and discussion of possible errors. Another recent paper[223] has described the use of potentiometric titration with sodium propoxide in propanol to study the acidity of alkylene phosphites, and has reached conclusions on the abnormally high acidity and other unexpected chemical features. Unfortunately, the account of the actual experiment is so condensed that assessment is extremely difficult. The acidity of dimethyl phosphite in its phosphorus(III) form appears unexpectedly low[225].

An unusual approach to estimating the acidity of phosphinylidene compounds is to determine J_{P-H} in the n.m.r. spectra, which depend on the *s* character of the phosphorus orbital involved in bond formation[226-228]. The acidity of dialkyl phosphites is apparent also in their interaction with trialkyl phosphites, which has been determined thermographically[229].

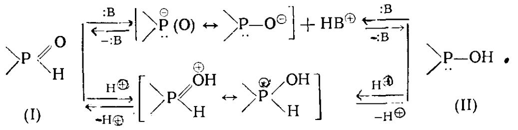
Little investigation has been made of the basicity of phosphinylidene compounds. Fluorosulphuric acid protonates dialkyl phosphites at the phosphinyl oxygen atom[230]; the process is monitored by n.m.r. Phosphinous acids are protonated considerably more readily; thus the first member of the series forms a hydrochloride stable at 50°C.[199]

Many phosphinylidene compounds form complexes with α-hydroxy-nitriles and other acidic alcohols, as is evident from the existence of azeotropes[231], and also with phenols and other compounds containing a mobile hydrogen atom[228,232-234]. The stability of the phenol complexes permits assessment of the electronic effect of substituents in the test compounds. Examination of this aspect reveals features of the various classes of phosphinylidene compounds[234]. The method enables the influence of stereochemical factors to be ascertained. Thus in six-membered cyclic phosphites the stability of complexes is determined by the orientation of the phosphoryl group. Certain judgments on the acid–base properties of dialkyl phosphites and several other phosphinylidene compounds can be based on study of the isotope effect in chemical shifts in n.m.r. spectra[40,235,236].

In connection with acid–base properties we must consider the association of phosphinylidene compounds, which depends significantly on their structure and sometimes also their stereochemistry. Dialkyl phosphites hardly associate at all[232,234]. Alkylene phosphites, in contrast, often form dimeric complexes[67,234,237,238]. It is interesting that six-membered cyclic phosphites with an equatorial phosphoryl group give more stable association complexes than do geometric isomers with an axial phosphoryl group[234]. Phosphorothiolites associate considerably more strongly than do phosphites[125].

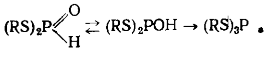
(*b*) Tautomerism of phosphinylidene compounds

The dyadic prototropy of these derivatives, whose study constitutes one of the classic problems of organophosphorus chemistry, has been discussed in detail in several reviews and monographs[239,240]. It is catalysed by acids and bases:



Dialkyl phosphites have been the most thoroughly investigated. At equilibrium they exist almost exclusively in form (I): kinetic data on deuterium exchange indicate that the concentration of form (II) reaches ~10^{-4}%. Phosphinylidene compounds containing substituents more electronegative than alkoxyl should contain more appreciable concentrations of form (II), which probably already applies to alkylene phosphites. The infrared spectrum of 1,2-dimethylethylene phosphite contains a band due to an acidic hydroxyl[72]. Potentiometric titration indicates that the series of five- and six-membered alkylene phosphites are real prototropic systems[233]. However, the preliminary character of the above studies must be borne in mind.

Cyclic ethylene phosphorothiolite has a considerable content of form (II).[128] Dialkyl phosphorodithiolites probably contain such a large quantity of form (II) that they summetrise spontaneously into phosphorotrithiolites[24,26,125]:



$$(RS)_2P(O)H \rightleftarrows (RS)_2POH \rightarrow (RS)_3P\ .$$

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‡Kinetic study of deuterium exchange has been used to compare the acidities of individual types of phosphinylidene compounds[194,198,224].

Bisthiocarbamoylphosphorodithiolites[241] and also phosphorodichloridous acid[24] undergo similar conversion. Phosphorodifluoridous acid is fairly stable[146]. This situation is consistent with the principles of prototropy: the aggregate electronic effect of fluorine on the polarity of the phosphorus–hydrogen bond is smaller than that of chlorine; hence the chloridous acid will have a greater content of form (II), which will undergo disproportionation.

The highest content (almost 100%) of form (II) has been found in bistrifluoromethylphosphinous acid[200]. Because of the stability of the phosphorus–carbon bond disproportionation does not take place. here. Unfortunately, synthetic investigations on fluorinated phosphinous acids are very few. Penta- and tetra-fluorinated dimethylphosphinous acids, which might be supposed to contain comparable contents of forms (I) and (II), have not yet been prepared.

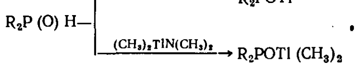
(*c*) Salt formation and complex formation

The tradition has become established in monographs and reviews on organophosphorus chemistry of not dealing separately with the preparation and properties of metal derivatives of phosphinylidene compounds, which are usually considered only as intermediate species in certain standard reactions. Interest in such derivatives, especially complexes of transition metals, has now increased sharply. Specific structural factors have been elucidated, and a catalytic effect has been detected[242-244].

The metal derivatives can be divided into salts and complexes, though the boundary is not always sharp. An alternative classification is based on the site—oxygen or phosphorus—at which the metal atoms are mainly localised. The latter scheme is adopted in the present Review.

Oxygen–metal derivatives. Alkali metals and their hydrides and alkoxides form with phosphinylidene compounds salts in which the phosphorus atom is usually three-coordinated[245]§. Salt formation is not accompanied by change in the configuration of the molecule[206,246,247]. Different phosphinylidene compounds react with metals at different rates: among the most reactive are dialkyl phosphites[206], while tetra-alkyldiamides of phosphorous acid are unreactive[248]. On treatment with Grignard reagents, however, the latter are smoothly converted into magnesium salts[193,248] having a phosphite type of structure.

Walther has prepared thallium(I) and thallium(III) derivatives of phosphinous acids[197,249,250]:



$$R_2P(O)H - \begin{cases} \xrightarrow{C_2H_5OTl} R_2POTl \\ \xrightarrow{(CH_3)_2TlN(CH_3)_2} R_2POTl(CH_3)_2 \end{cases} .$$

Titanium(IV) derivatives of these acids have been investigated¶. They were prepared not from the phosphinylidene compounds but from their ester[251] or anhydride[252] derivatives:

$$R_2POR' + TiCl_4 \rightarrow R_2P{-}OTiCl_3 .$$

Various complexes are formed by means of the phosphoryl oxygen. Thus dialkyl phosphites give interesting adducts with boron trifluoride[253].

Various physical methods have been used in a systematic investigation[254-257] of complexes with tin halides. The tendency to complex formation is determined by the structure of the ligands:

$$(RO)_2P(O)H < (RO)(R_2N)P(O)H < (R_2N)_2P(O)H \equiv R_2P(O)H .$$

Complexes of dialkyl phosphites with uranium have also been described[258]. Their structure, like that of many others, has been proved by comparing the infrared and n.m.r. spectra of the products with the corresponding spectra of the initial compounds.

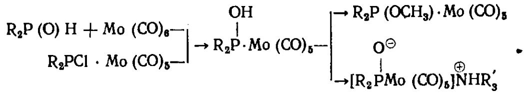
Phosphorus–metal derivatives. The *P*-mercuration of phosphinylidene compounds has been studied in detail. Biphosphinyl systems are formed by the action of mercury(II) oxide on dialkyl phosphites; if mercury halides are added to the reaction mixture, halogenomercuric derivatives separate[259,260]:

$$2(RO)_2P(O)H + HgO \rightarrow [(RO)_2P(O)]_2Hg \xrightarrow{HgX_2} 2(RO)_2P(O)HgX .$$

The structure of the products has been proved by n.m.r. and by X-ray diffraction[260,261]. Arsenation of phosphinous acids has been accomplished[249]:

$$R_2P(O)H + R'_2AsN(C_2H_5)_2 \rightarrow R_2P(O)AsR'_2 .$$

Molybdenum complexes have been obtained from the hexacarbonyl and phosphonous acids, as well as by the alkaline hydrolysis of chlorophosphine complexes of molybdenum pentacarbonyl; in these products phosphorus is attached to an acidic hydroxyl, which can be methylated with diazomethane or form salts with tertiary amines[262]:



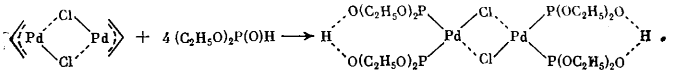
$$\left.\begin{matrix} R_2P(O)H + Mo(CO)_6 - \\ R_2PCl \cdot Mo(CO)_5 - \end{matrix}\right| \rightarrow \overset{OH}{\overset{|}{R_2P}} \cdot Mo(CO)_5 - \left|\begin{matrix} \rightarrow R_2P(OCH_3) \cdot Mo(CO)_5 \\ \rightarrow [R_2\overset{O^{\ominus}}{\overset{|}{P}}Mo(CO)_5]\overset{\oplus}{N}HR'_3 \end{matrix}\right. .$$

More complicated complexes of molybdenum with residues of dialkyl phosphites have been obtained from neutral phosphites that have undergone an Arbuzov type of rearrangement:

$$[(\pi\text{-}C_5H_5)Mo(CO)_3]_2 + P(OR)_3 \rightarrow (\pi\text{-}C_5H_5)Mo(CO)_2P(OR)_3P(O)(OR)_2 .$$

Neutral phosphonites are transformed similarly[263].

In the investigation of metal derivatives there has been a tendency during recent years to pay greater attention to elements of Group VIII. Strict structural data were first obtained by workers show showed[264] that dialkyl phosphites form complexes with simple palladium salts in which a new bond has been formed between the metal and a phosphorus atom bearing a free hydroxyl. New possibilities have since been demonstrated[243,265] for this process. Thus bis-π-allylpalladium dichloride forms a complex with diethyl phosphite in which the chloride bridges have been left undisturbed†:



The product is reduced by sodium tetrahydroborate to a mononuclear complex, which catalyses the hydrogenation of acetylenes, dienes, and aromatic nitro-compounds[243].

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§A recent paper suggests that the bonding of sodium may be determined by the nature of the solvent. In alcohol sodium is attached to phosphorus[209].

¶Attempts to obtain complexes from dialkyl phosphites and titanium tetrachloride led to degradative reactions[254].

†The n.m.r. spectra of this and similar compounds have been studied[266].

Analogous complexes have recently been prepared from the geometric isomers of 1-methyltrimethylene phosphite. Complex formation does not affect the configuration of the phosphorus atom. The stereoisomeric complexes differ in several properties. Reduction of the primary complexes may yield new, hydride complexes, whose catalytic activity is appreciably determined by their geometry[244]. Platinum complexes are obtained similarly to those of palladium. It has been proposed to prepare them from dialkyl or diaryl phosphites, phosphinous acids[265,267,268], or phosphonites[269].

The structure of complexes obtained from cobaltocene and dialkyl phosphites has been determined by X-ray examination[270]. On treatment with an acid a complex loses one cobalt atom, which can subsequently be replaced by another metal to give a polymetallic system[270,271]. Complexes of a different type have been prepared by reaction between dimethylglyoxime derivatives of cobalt and trimethyl phosphite; the process is accompanied by demethylation of the ester and complex formation between cobalt and phosphorus[272].

It has been proposed to apply an Arbuzov type of reaction to obtain dialkyl-phosphite[273] and phosphinous[197] complexes of dicarbonylcyclopentadienyliron from the corresponding neutral esters: for example

$$(\pi\text{-}C_5H_5)\,Fe\,(CO)_2Cl + P\,(OR)_3 \rightarrow (\pi\text{-}C_5H_5)\,Fe\,(CO)_2\,[P\,(O)\,(OR)_2] + RCl\ .$$

The ruthenium complexes have the most complicated structure, and are often formed in unusual ways. Thus reaction between dodecacarbonyltriruthenium and triaryl phosphites leads initially to partial displacement of carbon monoxide; further heating of the reaction mixture is accompanied by *o*-metallation and degradation of the phosphite ligand[274,275].

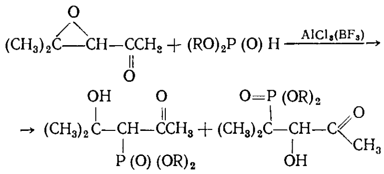
We finally note that complexes of phosphinylidene compounds are formed also by the action of diethyl phosphite on the Dewar form of tetrakistrifluoromethylthiophen, complex formation being due to isomerisation of thiophen into the usual form[276]. Complexes of dialkyl phosphites with hydrogen peroxide are also worthy of attention[277].

2. Substitution of Hydrogen Atom in Phosphinylidene Functional Group

(*a*) Electrophilic reactions

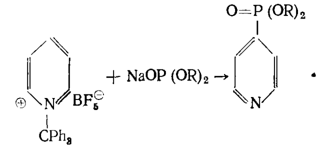
Alkylation and related processes. An important method for alkylating phosphinylidene anions is the Michaelis–Becker reaction[3]. Detailed investigation of its stereochemistry has shown that alkylation of salts of acid phosphonites[246,247] and of phosphinous acids[206] leaves the configuration at the phosphorus atom unchanged. Another group of studies of the dual reactivity of the anions has established that the direction of alkylation (at phosphorus or oxygen) may be determined by the chemical nature of the reagents[259,278] and by the solvation of the anion[279]. The influence of functional groups in the molecules on the ease of alkylation of the anions has been investigated, and in particular diaryl phosphites are found to act on α-chloro-isocyanates with remarkable ease: the reaction takes place without preliminary salt formation[280]. This has been established also for several hydroxy- and amino-benzyl systems[281–283]. Unusual conditions of alkylation apply to the use of sodium chloroacetate[284].

Special attention is merited by reactions of the Michaelis–Becker type in the presence of acid catalysts, which probably ensure regeneration of the tautomeric form of the phosphinylidene compound in which the phosphorus atom is tervalent. Moreover, these catalysts may activate also the alkylating reagents. An example is the action of dialkyl phosphites on epoxy-ketones[285]:



Study of the Michaelis–Becker reaction was initially directed mainly at the alkylating agents. In recent years investigation of the phosphorus component has developed. Thus the reaction has been extended to salts of amidic esters[286] and diamides[136,224] of phosphorous acid. Readily available magnesium salts can be used for alkylation of the latter[193], although exceptions are found[284].

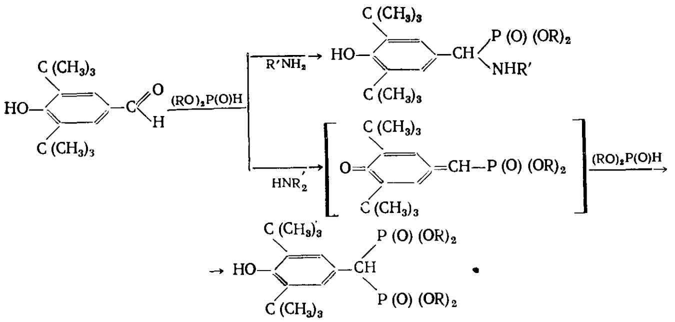
The reaction has been extended to aromatic systems. In liquid ammonia, aryl iodides react with salts of dialkyl phosphites when exposed to light of wavelength 350 nm.[287] Salts of *N*-oxides of pyridine and quinoline, as well as pyridinium salts, heteroarylate anions of dialkyl phosphites[288–290], with γ-regioselectivity observed for sterically hindered systems[290]:



The reaction between dialkyl phosphites and diazoacetic esters in the presence of copper sulphate is chemically cognate with the Michaelis–Becker reaction[34,35]. The first stage probably involves formation of a carbene, which deprotonates the phosphite, after which the classic scheme is followed.

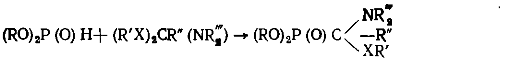
A large number of papers have been published on α-aminoalkylation, based on a reaction discovered in the early 1950s by Kabachnik et al.[291] and described somewhat later by Fields[292]. It consists in the simultaneous or successive action of ammonia (or a primary or secondary amine) on an oxo-compound and a phosphinylidene derivative. This synthetic method, which has come to be called the Kabachnik–Fields reaction, has found widespread and diverse use. Two trends characterise its development during recent years.

The first consists in the application of many types of phosphinylidene compounds and aminoalkylating agents. Good results are obtained by working not only with dialkyl phosphites and the other usual phosphinylidene compounds but also with dialkyl phosphites containing functional groups[19,25], with polyphosphites[97], monoalkyl phosphites[31], phosphonous acids[155], phosphinous acids[293–295], phosphorous acid[296–299], hypophosphorous acid[155,300] and its esters[216], and phosphorous amides[301]. Among aminoalkylating agents that have been used are hexamethylenetetramine[302] and other cyclic amines[303], oxazolidines[304], α-amino-peroxides[305], combinations of formaldehyde with sulphonamides[306] and of indol-3-ylacetaldehyde with amines[307], etc. The reaction has been extended to hydrazinoalkylation[157]. This method has its peculiarities: thus dialkyl phosphites react with 3,5-di-t-butyl-4-hydroxybenzaldehyde and primary amines according to the general scheme, but differently with morpholine and piperidine. It is assumed that in this case a quinoid intermediate is formed, which adds a second phosphite molecule[281]:



The second trend is to use the Kabachnik–Fields reaction to solve practical problems. It has now been employed for the production of important complexones[9,10,296,297,308], pesticides[309,310], flameproofing agents[306], intermediates in the synthesis of heterocycles[391], etc. Furthermore, complicated lactam antibiotics have been synthesised from α-amino-phosphonates[303].

Definite interest attaches to the α-alkoxy- and α-alkylthio-aminoalkylation of phosphinylidene compounds[311,312]:



$$(RO)_2P(O)H + (R'X)_2CR''(NR'''_2) \rightarrow (RO)_2P(O)C\begin{cases} NR'''_2 \\ -R'' \\ XR' \end{cases}$$

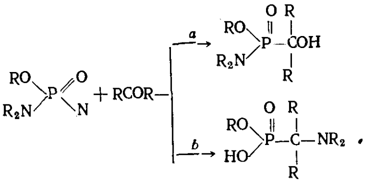
$X=O, S$.

The products react with dialkyl phosphites to give aminodiphosphonates. Phosphinous acids are immediately converted by bisdialkylaminoalkenes into aminodiphosphine oxides[311]. Acid phosphites and phosphonites react with orthoesters to form $\alpha\alpha$-dialkoxy-phosphonates and -phosphinates[313,314].

Addition to unsaturated polar compounds. The alkylation of phosphinylidene compounds by unsaturated polar compounds has proved synthetically very fruitful[2]. Conversions of this type are closely similar to the above and develop also by a carbonium mechanism.

Addition at the C=O bond. Phosphinylidene compounds undergo α-hydroxyalkylation on treatment with aldehydes and ketones. As a consequence of the work of Abramov (after whom the reaction is named) the method has been widely used. The main features‡ and the limits of applicability have now been determined, and the stereochemical direction of the reaction has been demonstrated[315]. The process usually occurs in the presence of bases, which convert the phosphinylidene compounds into the corresponding, highly nucleophilic anions. Kinetic study has shown a third-order reaction[316]. Recent results indicate[225] that addition of dimethyl phosphite at a carbonyl group in the presence of triethylamine occurs in the form $(CH_3O)_2.POH$, not as the anion $(CH_3O)_2PO^-$. Neutral phosphites as well as the usual bases can serve as catalysts[317]. Autocatalysis has been noted[201] in the addition of strongly basic phosphinylidene compounds, e.g. oxides of secondary phosphines. Bases are not employed with phosphonous acids[319]; acid catalysis probably occurs here, its role being to maintain the necessary concentration of the form of the phosphinylidene compound in which the phosphorus atom is tervalent. Acid catalysis operates also when neutral phosphinylidene compounds are used[320,321].

The Abramov reaction has been studied in greatest detail on dialkyl phosphites, partial phosphonites, and phosphinous acids[2]. Other classes of phosphinylidene compounds—diphosphites[84] and polyphosphites[88,97,322], phosphonous acids[189,300,319] and chlorides[189,323], phosphorous[324] and hypophosphorous[300] acids, alkyl dihydrogen phosphites[31,325], monoalkylphosphine oxides[162], monoalkyl hypophosphites[211,326,327], disilyl phosphites[328], phosphorodithiolites[125,128], and also diamides[241] and amidic esters[329,330] of phosphorous acid—have come to be used in recent years. With amides not only the classic reaction (*a*) but also the anomalous reaction (*b*) may occur[241,330]:



Route (*a*) is favoured by basic catalysts; reaction (*b*) occurs in their absence (further discussion of these reactions will be found below).

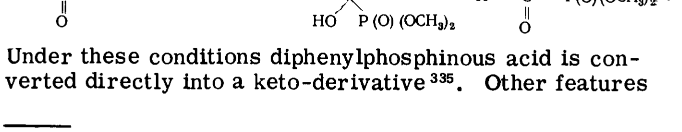
Several quantitative rules have been established for the reaction velocity: e.g. reactivity increases in the sequence

$$(RO)_2P(O)H < (RO)(R_2N)P(O)H < R_2P(O)H$$ [331].

Rates of conversion of dialkyl phosphites are hundredfold those for phosphorous acid[324].

Addition of phosphinylidene compounds to carbonyl compounds is reversible. It is often accompanied by secondary processes. α-Halogeno-carbonyl compounds with dialkyl phosphites are converted via a stage of halogenated α-hydroxy-phosphonates into enol phosphates; this reaction has been widely investigated and begun to be employed in industry[2,8]§. Rearrangement of non-halogenated hydroxy-phosphonates into phosphate systems began to be studied considerably later[2]. It is interesting that, depending on the quantity of basic catalyst present, the reaction of phosphinylidene with carbonyl compounds may or may not be accompanied by phosphonate–phosphate rearrangement[333].

Another type of rearrangement associated with the Abramov reaction is observed in the study of cyclic ketones. Thus tetraphenylcyclopentadienone and dimethyl phosphite in the presence of a tertiary amine or an alkoxide at 20°C give the hydroxycyclopentadienylphosphonate, which on further heating isomerises into a keto-phosphonate[334]:



Under these conditions diphenylphosphinous acid is converted directly into a keto-derivative[335]. Other features

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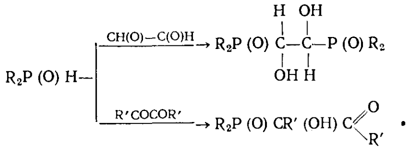
‡It must be remembered that the Abramov reaction may be accompanied by several side-processes, e.g.[318]

$$(C_6H_5)_2\dot{P}OLi + CH_3COCH_3 \rightarrow (C_6H_5)_2P(O)C(CH_3)_2CH_2COCH_3.$$

§Another type of reaction between dialkyl phosphites and α-halogenated carbonyl compounds is used in the preparation of $\alpha\beta$-epoxy-phosphonates[332].

of the reaction have been reported[336-339]. Additional complications may arise with high-temperature reactions (at 160–180°C). Thus the action of the anion of diphenylphosphinous acid on benzaldehyde and benzoylferrocene yields alkenes and their oxides[207]. Methylindanedione with dimethyl phosphite gives complicated di-indane systems[340].

The above facts do not diminish the merits of the Abramov reaction, but merely indicate how thoroughly it has been studied. During the past decade the reaction has found widespread use in the laboratory. Thus it has been applied to diverse carbonyl compounds, which has permitted development of a broad field in the chemistry of polyfunctional organophosphorus systems. Considering first the addition of phosphinylidene to dicarbonyl compounds, we note that glyoxal readily forms 1,2-diphosphinylethylene glycols with phosphinous acids, but α-diketones react differently[199]:

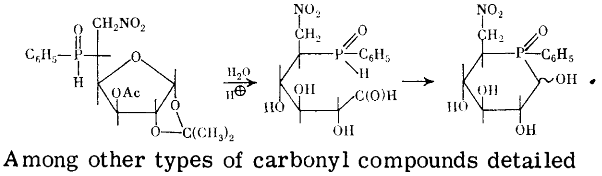


$$R_2P(O)H \xrightarrow{CH(O)-C(O)H} R_2P(O)CH(OH)-CH(OH)-P(O)R_2$$
$$R_2P(O)H \xrightarrow{R'COCOR'} R_2P(O)CR'(OH)C(=O)R' \; .$$

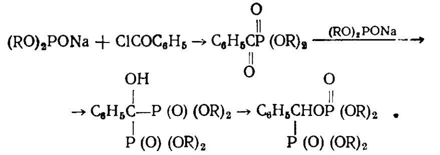
2-Methyl- and 2,2-dimethyl-indane-1,3-diones react similarly to α-diketones with dialkyl phosphites[340,341]. Several of the indane hydroxy-phosphonates obtained possess an anticonvulsant effect[341]. Pentane-2,4-dione yields 1 : 1 and 1 : 2 adducts depending on the proportions of the reactants; the latter adduct readily cyclises[342]. γ-Keto-aldehydes and γ-diketones on reaction with dialkyl phosphites and phosphinous acids give only 1,4-dihydroxytetramethylenediphosphonates (phosnin oxides).[343,344]

Reaction between dialkyl phosphites and epoxy-ketones leads to other complicated hydroxy-phosphonates[285]. Dihydroxy-phosphonates can be prepared from hydroxyketones[345]. Keto-acids and their esters have also been examined on treatment with various phosphinylidene compounds. The usual adducts are formed with temperature control[320,321], but phostones on heating[320,346]. The latter are obtained also by the action of phosphonous acids on $\alpha\beta$-unsaturated ketones[319].

During recent years the Abramov synthesis has been used in the study of carbohydrates. The reaction is applied either to the aldo-form of a monose[347-349] or to a cyclic keto-sugar[350,351]. An interesting case is the transcyclisation of an aldo-phosphonous acid[204]:

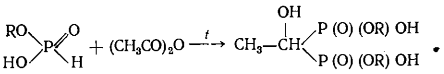


Among other types of carbonyl compounds detailed studies have been made on chlorides and anhydrides of carboxylic acids. With equimolecular proportions of the reactants and temperature control acid chlorides give α-oxo-phosphinyl derivatives on reaction with acid phosphites, phosphonites, and phosphinous acids[331,352,353]. In the presence of an excess of the phosphinylidene compound the reaction may develop further for example[352]:



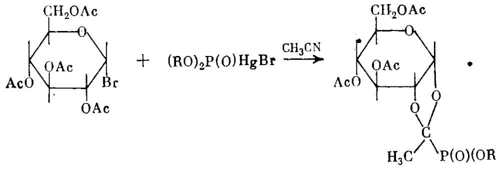
$$(RO)_2PONa + ClCOC_6H_5 \rightarrow C_6H_5C(O)P(O)(OR)_2 \xrightarrow{(RO)_2PONa}$$
$$\rightarrow C_6H_5C(OH)(P(O)(OR)_2)-P(O)(OR)_2 \rightarrow C_6H_5CH(P(O)(OR)_2)OP(O)(OR)_2 \; .$$

If excess of the acid chloride is used, it may acylate the initially formed oxo-phosphonate to a vinyl phosphonate[354]. Anhydrides of carboxylic acids react with oxides of secondary phosphines similarly to acid chlorides[355]. When anhydrides add to monoalkyl phosphites, the process develops differently, and the phosphonate–phosphate rearrangement does not occur[356][¶]:

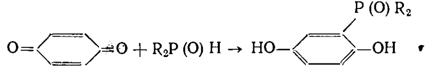


$$(RO)(HO)P(O)H + (CH_3CO)_2O \xrightarrow{t} CH_3-C(OH)H(P(O)(OR)OH)_2 \; .$$

Carboxylic esters do not usually add phosphinylidene compounds and their salts. However, Paulsen has shown[259] that tetra-*O*-acetyl-α-*D*-glucopyranosyl bromide is able to react with mercurated dialkyl phosphites:



The addition of phosphinylidene compounds to quinones has been subjected to detailed discussion. When dialkyl phosphites are used, monophosphinylated quinols are formed[358,359]. The reaction may be supposed to develop according to the classic scheme and to conclude in phosphonate–phosphate rearrangement. Hypophosphorous acid adds similarly to a quinone[115]. However, phosphinous acids behave abnormally[360,361]:



Among compounds in which the carbonyl group forms part of a cumulated system keten readily reacts with dialkyl phosphites to form α-oxo-phosphonates and their enol acetates[2]. Silylated and germylated ketens react somewhat differently with dialkyl phosphites and phosphinous acids[362]:

$$R_3ElCH{=}C{=}O + (R'O)_2P(O)H \xrightarrow{NEt_3} [R_3ElCH_2C(O)P(O)(OR')_2] \rightarrow$$
$$\rightarrow CH_2{=}C(OElR_3)P(O)(OR')_2$$
$$El = Si, Ge \; .$$

Reaction between phosphinylidene compounds and isocyanates has been studied more widely. In the presence of basic catalysts and tin derivatives dialkyl phosphites form carbamoylphosphonates[2,90,363,364]. Monoalkyl phosphites[325], acid phosphonites[365], oxides of primary phosphines[162], and magnesium[248] and silicon[366] derivatives of phosphorodiamidous acids react similarly. In the absence of bases dialkyl phosphites[367], phosphorothiolites[128], and diamides of phosphorous acid[241,248,368] may react differently, with preservation of the tervalent phosphorus atom. Under other conditions dialkyl phosphites and isocyanates give phosphoramidines[369].

Addition at the C=N bond. Phosphinylidene compounds undergo α-aminoalkylation by the action of azomethines and similar compounds. The reaction has been introduced into synthetic practice mainly by Pudovik, author of a series of experimental papers and a comprehensive

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[¶] The action of monoalkyl phosphites on carboxylic acid anhydrides does not always produce systems in which phosphorus–carbon bonds are preserved, as is indicated by the reaction of nucleoside phosphites[357]:

$$Nucl-O-P(=O)(H)OH + (CF_3CO)_2O \rightarrow Nucl-O-P(=O)(OH)OH \; .$$

general account[2]. Investigations on the catalysis (basic and acidic) and the kinetics of the reaction have established the influence of traces of moisture on its rate and other aspects[370-372].

The addition of phosphinylidene compounds at the C=N bond has broad synthetic value. Good results are obtained not only with dialkyl phosphites, acid phosphonites, and phosphinous acid[2] but also with phosphonous acids[10], hypophosphorous acid[373], monoalkyl phosphites[325], and diamides of phosphorous acid[248,301]. Various Schiff bases have been used, including those containing functional groups[374,375], derivatives of ferrocene[376] and carbohydrates[349,377], imino-chlorides[378], acylimines[379], alkoxyimines[380], chloroacylimines[280], etc. Usually systems with additional functional groups hardly differ from simple azomethines, but in some cases complications arise. Thus salicylideneamines often give poor results on reaction with dialkyl phosphites[381], probably owing to the electronic effects of the *ortho*-hydroxyl (cf. Ref. 281).

Addition of phosphinylidene compounds to azomethines accompanied by accumulation of more than one electron-accepting group on a single carbon atom may lead to rearrangement[378,382-384]:

$$C_6H_5N{=}C\,[P(O)R_2]_2 + R_2P(O)H \rightarrow C_6H_5NHC\,[P(O)R_2]_3 \rightarrow C_6H_5\overset{\overset{\displaystyle P(O)R_2}{|}}{N}{-}CH\,[P(O)R_2]_2\,.$$

A similar rearrangement takes place also with α-amino-phosphonates, if they have first been converted into sodium or potassium (but not lithium) derivatives[385].

Interesting preparations have been based on systems containing two azomethine groups—Schiff "bisbases"[156], hydrobenzamide[386], hydrazones[387], toluene-*p*-sulphonylhydrazones[388], and azines. In the latter case acid phosphites, phosphonites, and hypophosphites form 1 : 1 and 1 : 2 adducts[387,389,390]. Individual publications on this topic, e.g. Ref. 391, are open to objection. The observed formation of α-amino-phosphonates can be explained by the benzonitrile breakdown of hydrazones obtained in the first stage:

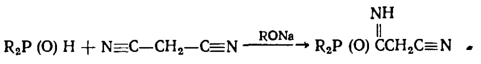
$$(C_2H_5O)_2P(O)\,CHPhNH{-}N{=}CHPh \xrightarrow{(C_2H_5O)_2PONa} \\ \rightarrow (C_2H_5O)_2P(O)\,CH(NH_2)\,Ph + PhC{\equiv}N\,.$$

Addition of phosphinylidene compounds to oximes is undoubtedly of synthetic interest. There was an indication that this reaction had been accomplished, but a later paper[392] has denied such a possibility.

Among systems containing a triple bond between carbon and nitrogen atoms aryl isocyanides react with dialkyl phosphites and phosphinous acids[380]:

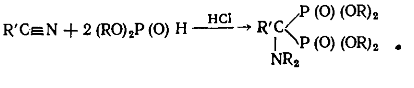
$$Ar\overset{\oplus}{N}{\equiv}\overset{\ominus}{C}{:} + {>}P(O)H \rightarrow {>}P(O)\,CH{=}NAr \xrightarrow{>P(O)H} [{>}P(O)]_2CHNHAr\,.$$

Nitriles add phosphonous acids in the presence of bases[393-396]: for example



$$R_2P(O)H + N{\equiv}C{-}CH_2{-}C{\equiv}N \xrightarrow{RONa} R_2P(O)\,\overset{\overset{\displaystyle NH}{\|}}{C}CH_2C{\equiv}N\,.$$

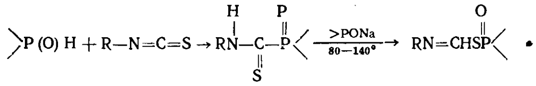
The second nitrile group is unaffected. Different assessments have been made of the possibility of the addition of dialkyl phosphites to nitriles, for a negative result[394] has been followed[397] by the positive result



$$R'C{\equiv}N + 2\,(RO)_2P(O)H \xrightarrow{HCl} R'\underset{\underset{\displaystyle NR_2}{|}}{C}\begin{matrix}{\nearrow}P(O)(OR)_2\\ {\searrow}P(O)(OR)_2\end{matrix}\,.$$

An important factor influencing the course of the reaction is acid catalysis; unfortunately, acids cause several complications, which make it difficult to assess the preparative merits of the method.

Addition at the C=S bond. Addition to isothiocyanates[2,325,398] recalls the corresponding preparation with isocyanates but differs in certain respects[366]. In several cases the addition of dialkyl phosphites and phosphinous acids to isothiocyanates concludes in rearrangement[399]:



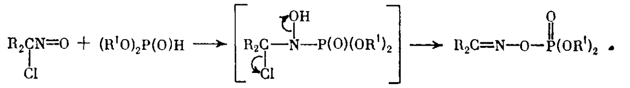
$$>P(O)H + R{-}N{=}C{=}S \rightarrow R\overset{\overset{\displaystyle H}{|}}{N}{-}\underset{\underset{\displaystyle S}{\|}}{C}{-}\overset{\overset{\displaystyle P}{\|}}{P}< \xrightarrow[80-140^\circ]{>PONa} RN{=}CHS\overset{\overset{\displaystyle O}{\|}}{P}<\,.$$

Addition to carbon disulphide[400]:

$$(RO)_2P(O)H + S{=}C{=}S \xrightarrow{NaOH} (RO)_2P(O)\,C(S)\,SNa$$

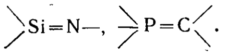
has been less investigated. The resulting salts would probably be promising for the production of organothiophosphorus compounds, including pesticides, complexing agents, oil additives, etc.

Addition at the N=O, S=O, and N=N bonds. Compounds containing these groups have been little investigated in their reactions with phosphinylidene compounds. Trifluoronitrosomethane adds to dialkyl[401] and monoalkyl[325] phosphites. If a nitroso-compound contains an α-chlorine atom, the process is more complicated[401]:



Addition at a S=O bond has been reported in the isolated examples of the reactions of dialkyl[402] and monoalkyl[325] phosphites with sulphur iminoxide. The action of dialkyl[403] and monoalkyl[325] phosphites on individual azo-compounds involves cleavage of the azo-bond.

In view of the tendency of modern chemical research to investigate complicated systems intermediate in nature between organic and inorganic we may suppose that comprehensive studies will be made in the near future on the addition of phosphinylidene compounds to unsaturated El=El′ bonds, e.g.



Addition to the C=C bond. Addition of phosphinylidene compounds at an electrophilic C=C multiple bond is a very common synthetic process[2]. During recent years especial attention has been paid to new aspects of its use. Thus the reaction has been extended to phosphinous[199,201] and phosphonous[319] acids, four-membered cyclic partial phosphonites[404], alkyl phosphorochloridites[142] and alkylphosphonous monochlorides[190], monoalkyl phosphites[325], phosphorothiolites[26], mono- and di-amides[224,286] of phosphorous acid, alkyl hypophosphites[212], and oxides of primary phosphines[162]. Rates of reaction of individual types of phosphinylidene compounds have been compared, and aspects of catalysis considered; rules already observed for addition to other electrophilic compounds are found to apply[224,405].

The range of unsaturated compounds that add phosphinylidene compounds is extremely wide—esters of unsaturated carboxylic acids[26,319]†, unsaturated heterocycles[375], nitro-compounds[406,407], fulvenes[408], allene-phosphonates[409] and other unsaturated phosphonates[410], and also 3,5-dinitrobenzoic acid[411]. Unfortunately, nitro-aromatic compounds have been little investigated in

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†The addition of dimethyl phosphite to perfluoroacrylic esters follows an unusual course[417].

this reaction, so that the wide opportunities for arylphosphonate synthesis and analysis of phosphinylidene compounds have not yet been realised.

Attention should be directed especially at unsaturated ketones and aldehydes, which, depending on the conditions and the catalysts used, can add phosphinylidene compounds not only at the ethylenic but also at the carbonyl bond[331,340,412–416]‡. It is significant that these reactions are subject to different types of control—kinetic at the carbonyl bond, but thermodynamic at the ethylenic bond[416]. The peculiarity of the addition of phosphinous acids and phosphonites having benzyl groups attached to the phosphorus atom is noteworthy[418].

Phosphinylidene compounds add to $C{=}C{-}\ddot{X}$ systems. During recent years investigations have been made on vinyl acetate[419], glycals[420], keten acetals[313], thioketen acetals and aminals[421], and amino- and alkoxy-acetylenes[422,423]. These reactions have been examined only in general outline.

Oxidation, addition of sulphur, imination, and related processes. Oxidation. Oxidation has been studied in connection with general aspects of the reactivity of phosphinylidene compounds and extension of the possibilities of organophosphorus synthesis. Many papers and patents have been published in which these compounds are intermediates in the production of acids containing quinquevalent phosphorus, including important technical products and natural compounds.

Dialkyl phosphites are oxidised to dialkyl phosphates by treatment with nitrogen dioxide[424,425]. The reaction has been extended to alkylene polyphosphites[87] and several other types of complicated derivatives. Other suggested oxidants are aqueous potassium permanganate[426] and oxygen in the presence of copper and vanadium catalysts[427]; in the latter case oxidation is complicated by dealkylation. Simple dialkyl phosphites have been oxidised with nitric oxide[428] and with 1,3-diphenyl-1,3-dithioacetone[429].

Acid phosphonites are oxidised more readily than are the corresponding phosphites, and phosphinous acids are still more easily oxidised; oxygen[201] or hydrogen peroxide[60] can be used as oxidant. It is interesting that diferrocenylphosphinous acid is comparatively inert towards oxidation[430].

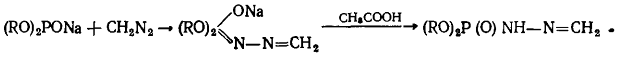
A fairly detailed study has been made of the oxidation of monoalkyl phosphites. Suggested oxidants are nitrogen dioxide[31], potassium permanganate[122], and mercury(II) chloride[117]. The oxidative phosphinylation of alcohols[431] and nucleosides[117,118,432] merits especial attention. Detailed investigations have been made on the oxidation of phosphonous acids, mainly with metal salts[433,434] but also with oxides of primary phosphines[162]. The oxidation of phosphorous amides by nitrogen dioxide involves rupture of the phosphorus–nitrogen bond[368].

Besides direct oxidation, indirect methods are often used, e.g. halogenation followed by hydrolysis. Despite the advantages of oxidation, it must be emphasised that frequently the suggested methods are not general in character. It is significant also that research is actually lacking on such current trends as catalysis on complexes, photochemistry, and in particular oxidation by singlet oxygen. Thus study of the oxidation of phosphinylidene compounds retains its urgency.

Addition of sulphur. Kabachnik et al. showed that dialkyl phosphites add sulphur in dioxan medium, and still more readily in the presence of tertiary amines[239]. Alkylene polythiophosphates[87] and cycloalkylene phosphorothioates have been prepared in this way[67,68]; retention of the configuration of the phosphorus atom has been established in the latter case. Dimethyl phosphite adds sulphur also on reaction with 1,3-diphenyl-1,3-dithioacetone[429]. Acid phosphonites also add sulphur in dioxan medium or in the presence of amines[172,435]. Retention of configuration by the phosphorus atom in this reaction has been demonstrated by the use of optically active phosphonites[180,436]. Phosphinous acids add sulphur with evolution of heat[201,430]. Phosphorous diamides[286] and amidic esters[437] react less vigorously with sulphur.

Phosphinylidene compounds add also selenium under conditions similar to the above[67,68].

Imination. The first results on this process were obtained by Kabachnik et al., who treated salts of dialkyl phosphites with diazomethane[239]:



$$(RO)_2PONa + CH_2N_2 \rightarrow (RO)_2P\langle{}^{ONa}_{N-N=CH_2} \xrightarrow{CH_3COOH} (RO)_2P(O)NH{-}N{=}CH_2 .$$

Pudovik et al.[439] have observed similar reactions between diethyl phosphite or its trialkylsilyl derivative and diazoacetic ester. The reactions of diphenyl phosphite[239] and also of trialkylsilyl derivatives of dialkyl phosphites[440] with phenyl azide can probably be included in this group. Azo-coupling occurs similarly[403,441]:

$$(RO)_2P(O)H + ArN_2^{\oplus} \rightarrow (RO)_2P(O)N{=}N{-}Ar .$$

Halogenation. Phosphorous diesters are readily converted by chlorine into phosphorochloridates. The reaction is strictly stereodirected with retention of configuration by the phosphorus atom[77,315], and has been extended to more complicated compounds, including various types of polyphosphites[85,89]. Chlorination can be effected also by sulphuryl chloride[102], chlorosuccinimide[77], and copper(II) chloride[442]. Acid phosphonites[171] and thiolic[125] and amidic[286] esters of phosphorous acid undergo similar chlorination. With monoalkyl phosphites chlorination is completed by anhydridisation; when the reaction is conducted in water, monoalkyl phosphates separate[31].

Fluorination (by means of a perchloryl fluoride)[443], bromination[33], and thiocyanation[444] of phosphinylidene compounds have been reported, but development of these processes has been slight, probably because of experimental complexity.

Todd–Atherton reaction. This reaction provides a very convenient and effective method for the oxidative phosphinylation of nucleophiles by the action of a phosphinylidene compound, tetrachloromethane (or similar halide), and a base[445]. The first stage can be written

$$\rangle P(O)H + CCl_4 + B \rightarrow \rangle P(O)Cl + HCCl_3 + HCl\cdot B .$$

If nothing more is added to the mixture, an acid chloride is formed[240]. This process has advantages over other methods for the preparation of phosphorus acid chlorides. If, however, a nucleophile is also added to the reaction mixture, phosphinylation takes place.

The Todd–Atherton reaction has been applied not only to simple dialkyl phosphites but also to hydroxyalkyl and other functionally substituted phosphites[19,25,45,66], diphosphites[446], polyphosphites[97,102], acid phosphonites[181,447,448], diphosphinites[170], phosphonous acids[449,450], amides of

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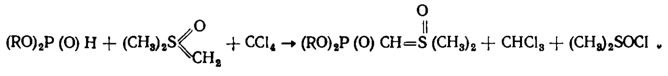
‡See also the comments on quinones and cyclic ketones in the above paragraphs on the C=O system.

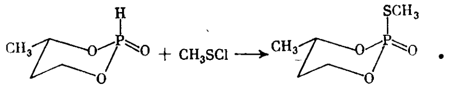
phosphorous acid[138,139,446], monoalkyl phosphites[33], and hypophosphorous acid[450] and esters[215,217]. The popularity of the reaction is due also to the wide range of nucleophiles used—alcohols and phenols[45,451], water[450], amines, which may be functionally substituted and heterocyclic[19,138,446,452], esters of amino-acids[453], hydroxylamine[454], oximes[455], silyl vinyl ethers[456], oxiran[448], etc. An unusual and interesting process is the *C*-phosphinylation of dimethylsulphoxonium methylenylide[457]:



$$(RO)_2P(O)H + (CH_3)_2S\begin{smallmatrix}\nearrow O\\ \searrow CH_2\end{smallmatrix} + CCl_4 \rightarrow (RO)_2P(O)CH{=}\overset{\overset{O}{\|}}{S}(CH_3)_2 + CHCl_3 + (CH_3)_2SOCl\ .$$

Zwierzak has recently begun to study the Todd–Atherton reaction in a two-phase system with quaternary ammonium salts as catalysts[458]. This variant of the reaction has great advantages for preparative purposes and shows promise for industrial application.

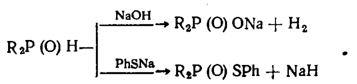
Thiolation. Phosphinylidene compounds are converted into thiolophosphoric esters by the action of organic sulphenyl chlorides, thiocyanates, and disulphides and of sulphenamides. The configuration of the phosphorus atom is preserved during thiolation: for example[459]



The reaction is of general value, and applies to acid phosphites[88,460], acid phosphonites[435], phosphinous acids[192], and monoalkyl phosphites[113]. Among the latter have been investigated nucleoside phosphites, which with diphenyl sulphide give nucleoside phosphorothiolates, of interest as reagents for producing an internucleotide bond. When disulphides are used, the composition of the reaction mixture must always be strictly controlled, the possibility of a secondary process being taken into account[461].

(*b*) Nucleophilic reactions

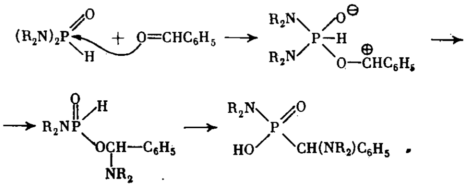
It is unlikely that a general reaction with nucleophiles will be discovered for phosphinylidene compounds. Indeed, when these compounds are esters, bifurcation occurs: both the phosphorus atom and the ester carbon atom are attacked, leading to dealkylation in the latter case. Attack on phosphorus by a nucleophile containing mobile hydrogen involves preferential displacement not of hydrogen but of an alkoxide ion: i.e. phosphinylation will occur without significant change in the nature of the phosphorus compound. When amidic or thiolic phosphinylidene compounds are used, phosphinylation of a nucleophile containing mobile hydrogen will become still more dominant. The best compounds for the investigation of nucleophilic hydrogen substitution are thus phosphinous acids[360]:



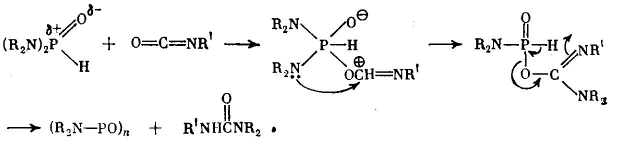
$$R_2P(O)H - \left| \begin{array}{l} \xrightarrow{NaOH} R_2P(O)ONa + H_2 \\ \xrightarrow{PhSNa} R_2P(O)SPh + NaH \end{array} \right. .$$

The reaction with alkali was subsequently extended to other compounds[462,463].

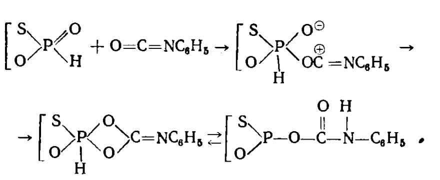
Certain complicated reactions between amides of phosphorous acid and carbonyl compounds probably begin with nucleophilic attack on the phosphorus atom: for example[241]



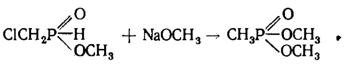
Although not all aspects of this reaction have yet been studied, an intermediate incorporation stage has already been established by nuclear magnetic resonance. The possibility of the incorporation of two molecules of the carbonyl compound has also been demonstrated[241,368]. The reaction of amides of phosphorous acid with isocyanates obviously involves a similar transformation, which has an unusual conclusion[241,248,368]:



Incorporation of carbon disulphide at a phosphorus–nitrogen bond may be supposed to develop similarly[241]. The "anomalous" action of phenyl isocyanate on ethylene phosphorothioite[128] and dimethyl phosphite[367] is more problematic, but even here the first stage probably consists in nucleophilic attack by oxygen on phosphorus:



The interaction of α-substituted phosphonous acids[464] and their partial esters[465] with nucleophiles is probably of the same type: for example



$$ClCH_2P\begin{smallmatrix}\nearrow O\\ \leftarrow H\\ \searrow OCH_3\end{smallmatrix} + NaOCH_3 \rightarrow CH_3P\begin{smallmatrix}\nearrow O\\ \leftarrow OCH_3\\ \searrow OCH_3\end{smallmatrix}\ .$$

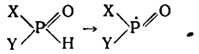
Such reactions have no general significance: chloromethylphosphonous acid reacts with ammonia to give aminomethylphosphonous acid[466].

On the whole the action of nucleophiles on phosphinylidene compounds has been little investigated. Papers have been concerned mainly with the preparative aspect, while the chemistry of the processes has been discussed seldom and usually only speculatively. Nevertheless, what has been done is very valuable, since it relieves us of a certain monotony in the development of the chemistry of phosphinylidene compounds and opens up great prospects for synthetic work.

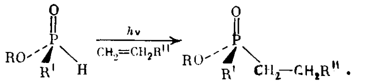
(*c*) Radical reactions

The ever increasing interest taken in radical processes in organic chemistry is evident also in the present field. The most systematic study has been made of the addition of phosphinylidene compounds to alkenes. Features and possibilities of this reaction have been surveyed in a recent monograph[467], so that here we shall consider only fundamental papers and also the most recent publications.

In the addition of phosphinylidene compounds to alkenes radicals can be generated by chemical[468,469], photochemical[470], or radiation-chemical[471-473] methods:

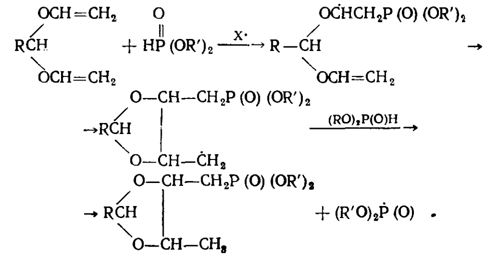


The structure of phosphoranyl radicals has been clarified in the course of a recently concluded controversy[468,469,471]. The resulting radicals are able to preserve the configuration of the initial phosphinylidene compounds, which enables optically active organophosphorus compounds to be synthesised[436]:



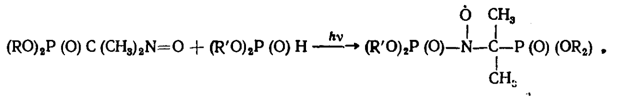
The ideas of dynamic stereochemistry have been extended to other aspects of radical addition. Thus it has been found that the conformational state of the original phosphinylidene compound governs its reactivity[468].

Synthetic investigations have been widely developed. Alkyl hypophosphites have also been brought into reaction with alkenes; under the given conditions addition occurred only once[215]. In the early work homolytic addition was applied almost exclusively to alkenes, but subsequently perfluoroalkenes[474], unsaturated heterocycles[470,475], allylic derivatives of heterochain polymers[152], etc. have been used. Diene systems exhibit noteworthy behaviour: for example[199,476]:



Cyclisation is akin to telomerisation[478] and the radical rearrangements observed in the addition of dialkyl phosphites to certain terpenes[477].

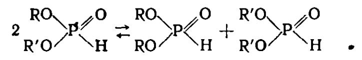
Under the conditions of radical reactions phosphinylidene compounds are able to phosphinylate aromatic compounds[479] and add to acetylene in the presence of transition-metal complexes as catalysts[480]. Homolytic addition is especially interesting in cases in which the heterolytic process cannot be accomplished, as in the recently discovered reactions with nitroso-compounds[481,482], nitro-compounds[483], and oximes[483]: for example



$$(RO)_2P(O)C(CH_3)_2N{=}O + (R'O)_2P(O)H \xrightarrow{h\nu} (R'O)_2P(O){-}\underset{\dot{O}}{N}{-}C(CH_3)_2{-}P(O)(OR_2)\ .$$

3. Reactions Not Involving the Phosphinylidene Functional Group

Phosphinylidene compounds in which the phosphorus atom is attached to electron-accepting groups are widely used in phosphinylation, e.g. in transesterification. The possibilities and peculiarities of such reactions have already been discussed in Section II. A somewhat related process is disproportionation, i.e. exchange of substituents at the central functional group. Thus unsymmetrical dialkyl phosphites give two new symmetrical esters even on storage[18], and this process may be reversed[484]:



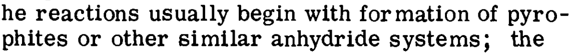
More complicated cases of disproportionation involve the cyclisation of diphosphites[83] and the oligomerisation of alkylene phosphites[71,74]. The mechanism of disproportionation has not been investigated; it is most likely catalysed by traces of alcohols or other compounds having a mobile hydrogen atom and capable of forming labile adducts with phosphinylidene compounds.

A second type of reaction is exemplified by dealkylation of the esters, which has been studied almost exclusively on dialkyl phosphites. The kinetics and the mechanism have now been studied under conditions of acid and alkaline hydrolysis[485] and treatment with metal salts[116,486]. Dealkylation of dialkyl phosphites is used in the preparation of monoalkyl phosphites (Section II), which include products of practical importance[487]. Isolated results have appeared on the dealkylation of partial phosphonites[488], which resemble dialkyl phosphites in this respect.

4. Reactions with Decrease in Coordination of Phosphorus

Reactions in which phosphinyl (phosphinothioyl, phosphinimidyl) groups are formed are usually preferable in the chemistry of organophosphorus compounds. Especial interest therefore attaches to the opposite reactions, which have been studied in greatest detail for phosphinylidene compounds.

Treatment of phosphonous and phosphinous acids with phosphorus trichloride gives the corresponding acid chlorides[149,489]:



$$(C_6H_5)_2P(O)H + PCl_3 \rightarrow \left[(C_6H_5)_2\underset{H}{\overset{\oplus}{P}}{-}OPCl_2Cl^{\ominus}\right] \rightarrow (C_6H_5)_2PCl + [HOPCl_2]\ .$$

Alkylene phosphites react similarly with the trichloride[490], and also dialkyl phosphites and other phosphinylidene compounds with dialkyl phosphorochloridites[141,491,492]: for example

$$(RO)_2P(O)H + (R'O)_2PCl \rightleftarrows (RO)_2PCl + (R'O)_2P(O)H\ .$$

The equilibrium can be displaced by distilling off the volatile product.

The reactions usually begin with formation of pyrophosphites or other similar anhydride systems; the hydrogen chloride liberated then degrades the primary product in conformity with an Arbuzov reaction, forming either the initial or new products. If reaction occurs in the presence of a base, the anhydride can be isolated[141,491]. Anhydrides can be obtained also by several related methods[491,493]. It is very important that phosphinylidene compounds (or their salts) can be phosphinylated not only at oxygen but also at phosphorus[141,491]§: for example

$$PCl_3 + 3\,(RO)_2P(O)H \xrightarrow{C_5H_5N} P\,[P(O)(OR)_2]_3\ .$$

P-Phosphinylation occurs also when phosphinous acids are treated with acetic anhydride[494] or silicon tetrachloride[495]. In most cases chlorosilanes[496,497], like silylamines[133,498,499] give with phosphinylidene compounds silyl

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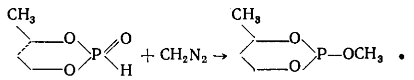
§ In some cases the direction of phosphinylation is determined by steric factors[491].

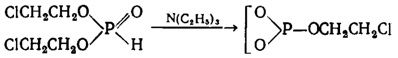
phosphites. The latter are of great interest, e.g. in the chemistry of nucleic acids[497]. Phosphonous acids react similarly with silylating reagents[106,187,500]; intramolecular silylation is possible here[187].

Reaction with aliphatic diazo-compounds was first studied on 1-methyltrimethylene phosphite treated with diazomethane and compounds containing mobile hydrogen as catalysts[446]:

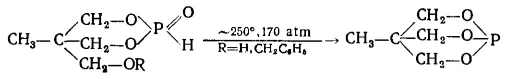


Fresh examples of this reaction have recently been given[501] with discussion of further reactions in the system comprising cyclic phosphite and diazo-compound. The reaction of 3-hydroxy-2.2-dimethylpropyl hypophosphite with diazomethane to yield the cyclic neutral 2,2-dimethyltrimethylene hypophosphite is of fundamental interest[217].

The ready intramolecular *O*-alkylation of bis-2-chloroethyl phosphite[502]



is noteworthy. The cyclisation[42,503]

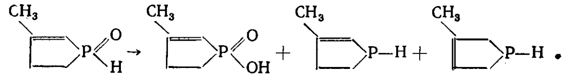


can be regarded as of the same type. One factor governing these not altogether usual transformations is evidently preferential formation of cyclic and bicyclic phosphite structures.

Several other reactions involving a decrease in the coordination number of the phosphorus atom have been considered above.

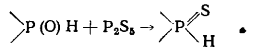
5. Other Reactions of Phosphinylidene Compounds

Investigations of the redox disproportionation of phosphinylidene compounds, begun earlier[240], have been continued during recent years. New cases of disproportionation have been found, concluding in peculiar chemical phenomena, e.g. isomerisation of one of the products[202]:



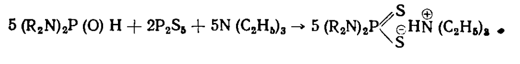
Studies have begun on the disproportionation of alkyl hypophosphites[213,327] and pyrophosphonous acids[504]. A distinguishing feature of this work is clarification of the destiny of the phosphorus intermediates; phosphenes $R\ddot{P}$ have been examined in greatest detail—the rules of their oligomerisation and other transformations.

Phosphorus pentasulphide may convert phosphinylidene compounds into phosphinothioylidene derivatives:



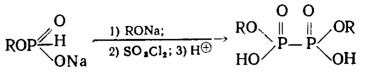
$$>P(O)H + P_2S_5 \rightarrow >P(=S)H \; .$$

The replacement of oxygen by sulphur involves no significant change in configuration of the phosphorus residue[179]. When amides of phosphorous acid are used, products containing two sulphur atoms are formed[505]:



$$5\,(R_2N)_2P(O)H + 2P_2S_5 + 5N(C_2H_5)_3 \rightarrow 5\,(R_2N)_2P(=S)S^{\ominus}\,\overset{\oplus}{H}N(C_2H_5)_3 \; .$$

An unusual reaction for phosphinylidene compounds occurs[506] when salts of monoalkyl phosphites are treated successively with an alkoxide, sulphuryl chloride, and an acid to give acid hypophosphites:



In conclusion it may be noted that the chemistry of phosphinylidene compounds, established as early as the nineteenth century, continues its successful development. One reason for such "longevity" is the appearance of fertile trends, such as steric regulation of reactions and investigation of the structure and catalytic properties of metal derivatives. At the same time the classic problems are acquiring a fresh interpretation and development by the application of modern physical methods and theoretical views. As a consequence these problems are beginning to interlock with new trends, which holds promise for further development in this field of chemistry.

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Combined Inhibition of Cholinesterases by Organophosphorus Compounds

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The review is devoted to studies on the combined inhibition of the catalytic activity of cholinesterases by organophosphorus compounds. This type of inhibition depends significantly on the presence of hydrophobic substituents in the organophosphorus molecule. It is suggested that there is a possibility of "concerted" or "non-concerted" sorption of the hydrophobic groups of the inhibitor on the hydrophobic regions in the vicinity of the anionic and esterase sites on the active surfaces of cholinesterases. These effects apparently determine the nature of the inhibition of cholinesterases.
The bibliography includes 44 references.

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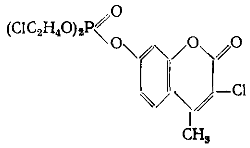
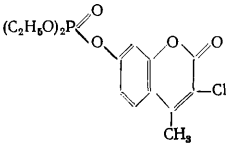
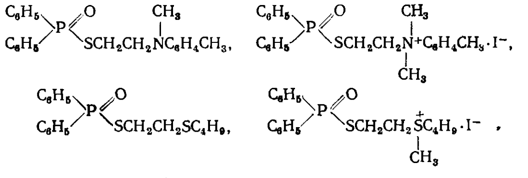
I. INTRODUCTION

The esters of phosphorus(V) acids, which exhibit a phosphorylating capacity, are known to be capable of inhibiting cholinesterases—vitally important enzymes which regulate the transmission of nerve excitation from the nerve to the innervated cell. Until recently it was believed that organophosphorus compounds are capable of only irreversible inhibition of cholinesterases by phosphorylating the serine hydroxyl, which forms part of the esterase centre in these enzymes. However, in 1969, Aldridge and Reiner[1] observed in experiments with coumarinyl phosphates (I) and (II) two types of inhibition of the catalytic activity of acetylcholinesterase (ACE) of bovine erythrocytes: (a) irreversible inhibition progressing in the course of time, and caused by the phosphorylation of the active centre of the enzyme; (b) reversible inhibition established instantaneously and non-progressive. According to the authors[1], the latter type of inhibition is associated with the interaction of the organophosphorus inhibitor (OPI) with the section of the active surface of the enzyme responsible for the inhibition of the activity of ACE by the excess of substrate.


(I)


(II)

In 1971, a similar complex type of inhibition of catalytic activity was observed by Kabachnik and coworkers for another enzyme—butyrylcholinesterase (BuCE) of horse blood serum, in experiments with certain diphenylphosphinothiate esters:



Since inhibition of activity by the excess of substrate is not characteristic of BuCE, the authors[2] explained the presence of the reversible component in the enzyme inhibition by the possibility of the "non-productive" sorption of the inhibitor on the active surface of the enzyme (E), which does not entail the orientation of the inhibitor on the active surface of BuCE favourable for the phosphyrylation of the serine hydroxyl. The authors suggested that the enzyme–inhibitor complex (EI_r) formed is incapable of subsequent conversion into the phosphorylated enzyme (EIn′), in contrast to the usual Michaelis type complex (EIn): it is analogous to the enzyme–inhibitor complex obtained when cholinesterases are acted upon by reversible inhibitors, for example tetralkylammonium ions†. In other words, instead of the usual phosphorylation mechanism

$$E + In \rightleftarrows EIn \xrightarrow{k_2} EIn' ,$$

the following mechanism has been proposed for this complex and so-called combined type of inhibition[2]:

$$E + In - \begin{cases} \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} EIn \xrightarrow{k_2} EIn' \\ \overset{K_{i,r}}{\rightleftarrows} EI_r \end{cases} ,$$

where k_1, k_{-1}, and k_2 are the rate constants for the corresponding reaction stages and $K_{i,r}$ is the equilibrium dissociation constant of the "non-productive" complex EI_r.

Combined inhibition is manifested primarily by the fact that, with increase of the inhibitor concentration [In], there is a significant decrease of the experimental bimolecular rate constant for the phosphorylation of the enzyme k_{II}, which is calculated from the equation

$$k_{II} = \frac{1}{[In]\,t} \ln (v_0/v_t),$$

where v_0 is the rate of the enzymatic hydrolysis of the substrate in the absence of the inhibitor and v_t the rate (after t min) of incubation of the enzyme with the inhibitor S, the concentration of which is many times greater than

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† The extensive experimental data available at the present time permit the hypothesis that the complex EI_r does not differ significantly from the complex EIn, and may consist of a section of the enzyme–inhibitor complex which does not enter into the enzyme phosphorylation reaction. We shall therefore henceforth regard the complex EI_r as "non-productive" and the complex EIn as "productive".

the enzyme concentration. Reversible inhibition by these compounds is manifested both in the phosphorylation of the enzyme, where it is estimated in terms of the equilibrium inhibitor constant $K_{i,r}$, and in the enzymatic hydrolysis of the substrate (acetylcholine), where it is estimated in terms of the constant $K_{i,S}$.

The most reliable parameter of the combined inhibition is the decrease of the catalytic activity of the enzyme when $t \to 0$.

In order to calculate the rate constants for the irreversible inhibition of BuCE and ACE and of the equilibrium constants $K_{i,S}$ and $K_{i,r}$, the following equations were used[2]:

$$k = \frac{1}{[\mathrm{In}]\, t}\left(\ln\frac{v_0}{v_t} - \ln\frac{v_0}{v_{0,i}}\right),$$

where k is the experimental bimolecular rate constant for the given value of t, and $v_{0,i}$ the rate of the enzymatic hydrolysis of acetylcholine in the presence of the inhibitor at zero time of the incubation with the enzyme:

$$K_{i,S} = \frac{K_m}{(K_m + [S])[v_0/(v_{0,i} - 1)]},$$

where K_m is the Michaelis constant and [S] the substrate concentration. The true bimolecular rate constant k_a, which is independent of the inhibitor concentration, and the inhibitor constant $K_{i,r}$ were determined graphically from the values of k for different [In] using the relation

$$k = \frac{k_a}{1 + K_{i,r}}.$$

A study of the kinetics of the interaction of BuCE with diphenylphosphinothioate esters[2] yielded data in good agreement with mechanism (2) and the equations which followed from it. This first study initiated a detailed investigation of the relation between the chemical nature of OPI and their ability to inhibit cholinesterases via the combined mechanism.

Preparations of butyrylcholinesterase (BuCE, CE 3.1.1.3) from horse blood serum and of acetylcholinesterase (ACE, CE 3.1.1.7) from human blood erythrocytes were used. The enzyme activities were determined from the rate of hydrolysis of acetylcholine chloride or acetylcholine iodide (AX).

Table 1. Constants for the inhibition of BuCE by the compounds $(C_6H_5)_2P(O)SCH_2CH_2R$ (A) and $(C_6H_5)_2P(O)OCH_2 . CH_2R$ (B).[2]

R	$10^{-5}\ k_a$, litre mole^{-1} min^{-1}	$10^7\ K_{i,r}$, mole litre^{-1}	$10^7\ K_{i,S}$, mole litre^{-1}	$10^6\ K_i$, mole litre^{-1}
		A		B
SC_4H_9	0,25	21	33	12
$^+S(CH_3)C_4H_9 \cdot I^-$	15	4,8	2.4	1,8
$N(CH_3)C_6H_4$ (*m*-CH_3)	0,05	0.41	13	3,9
$^+N(CH_3)_2C_6H_4$ (*m*-CH_3)$\cdot I^-$	10	0.55	0,8	0,58

The rate of hydrolysis of AC under the influence of BuCE and ACE were determined by potentiometric titration of the acetic acid formed in the reaction at a constant pH (7.5 or 7.8) using pH-meters with glass electrodes[3,4]. In the study of the inhibition of the catalytic activity of cholinesterases by purely reversible inhibitors, the inhibitor constants K_i were determined by a graphical method[5]. The results of these studies are described in the present review.

II. INTERACTION OF CHOLINESTERASES WITH DIPHENYLPHOSPHINOTHIOATE ESTERS

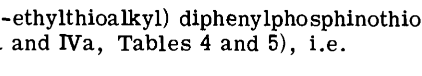
As stated above, Kabachnik and coworkers[2] investigated the inhibition of BuCE by certain diphenylphosphinothioate esters (Table 1).

The phosphinothioates investigated proved to be strong inhibitors of BuCE with a combined activity. The bimolecular irreversible inhibition rate constants obtained for them are close to the values for the analogous *OO*-diethyl *S*-alkylphosphorothioates and *O*-ethyl *S*-alkyl methylphosphonothioates[6,7]. In terms of their reversible activity, they are greatly superior to typical reversible inhibitors such as tetra-alkylammonium ions[8]. The inhibitor constants of the phosphinothioates are smaller approximately by an order of magnitude than the values of K_i for their oxygen analogues, which are also powerful but only reversible inhibitors (Table 1). Thus both phosphinothioates and their oxygen analogues are capable of forming very stable enzyme–inhibitor complexes, probably because of the presence in their composition of two or three phenyl groups, which greatly intensify the hydrophobic interaction of OPI with BuCE, the latter having comparatively large hydrophobic regions in the vicinity of both the anionic and the esterase sites[9-11].

The reversible inhibition by the phosphinothioates investigated is of a competitive type, as shown by the constancy of $K_{i,S}$ calculated by Eqn.(14) for different [In] and by the direct proportionality between $1/k$ and [In]. When [S] is reduced by a factor of 20 for a given [In], the slope remains the same (Fig.1), but the intercept *b* diminishes, i.e. the substrate exhibits a protective function in relation to the reversible inhibition of the enzyme, which is again characteristic of competitive inhibition.

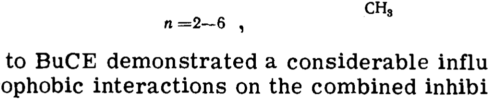
There is a definite relation between the phosphorylation rate constants k_a and the equilibrium dissociation constants of reversible enzyme–inhibitor complexes ($K_{i,S}$ and $K_{i,r}$): the higher the value of k_a, the lower the constants $K_{i,S}$ and $K_{i,r}$, i.e. the more stable are the complexes. Inhibitors with cationic groups have higher values of k_a and lower values of $K_{i,S}$ and $K_{i,r}$ than "uncharged" compounds.

The data obtained in the study of the inhibiting activity of *S*-(β-alkylthioethyl) diphenylphosphinothioates and their methiodides[12,13] (series Ia and IIa, Tables 2 and 3), i.e.



$R = CH_3—C_6H_{13}$,

as well as *S*-(ω-ethylthioalkyl) diphenylphosphinothioates[14,15] (series IIIa and IVa, Tables 4 and 5), i.e.



$n = 2—6$,

in relation to BuCE demonstrated a considerable influence of the hydrophobic interactions on the combined inhibition. It follows from Tables 2 and 3 that, with increase of the length of the alkyl group attached to sulphide or sulphonium sulphur (series Ia and IIa), a continuous increase of both irreversible (increase of k_a) and reversible (decrease of $K_{i,S}$ and $K_{i,r}$) inhibition of the catalytic activity of BuCE is observed[13]. An analogous increase of inhibition with increase of the distance between the phosphorus and sulphide or sulphonium sulphur atoms in compounds of series IIIa and VIa (Tables 4 and 5) has also been noted[15]. A characteristic feature is that, with increase of the P–S distance, the irreversible inhibition hardly changes (series IIIa, Table 5) or diminishes, particularly at the beginning as n increases from 2 to 3 (Table 5).

Table 2. Constants for the inhibition of BuCe by the compounds $(C_6H_5)_2P(O)SCH_2CH_2SR$ (series Ia) and $(C_6H_5)_2P(O)OCH_2CH_2SR$ (series Ib).[13]

R	$10^{-4}k_a$, litre mole^{-1}	$10^6K_{i,r}$, mole litre^{-1}	$10^6K_{i,S}$, mole litre^{-1}	10^6K_i, mole litre^{-1}
	series Ia			series Ib
CH_3	0.33	9.3	11	28
C_2H_5	0.42	7.2	7.3	23
C_3H_7	0.77	3.6	4.1	16
C_4H_9	2.5	2.1	3.4	8.4
C_5H_{11}	7.2	0.90	0.95	4.0
C_6H_{13}	13	0.55	0.48	1.2

Table 3. Constants for the inhibition of BuCE by the compounds $(C_6H_5)_2P(O)SCH_2CH_2\overset{+}{S}(CH_3)R.I^-$ (series IIa) and $(C_6H_5)_2P(O)OCH_2CH_2\overset{+}{S}(CH_3)R.I^-$ (series IIb).[13]

R	$10^{-5}k_a$, litre mole^{-1} min^{-1}	$10^7K_{i,r}$, mole litre^{-1}	$10^7K_{i,S}$, mole litre^{-1}	10^6K_i, mole litre^{-1}
	series IIa			series IIb
CH_3	3.0	14	6.6	16
C_2H_5	4.9	10	4.4	13
C_3H_7	6.7	6.1	2.7	6.7
C_4H_9	15	4.8	1.2	1.8
C_5H_{11}	22	3.1	0.89	0.94
C_6H_{13}	27	1.2	0.56	0.51

Table 4. Constants for the inhibition of BuCE by the compounds $(C_6H_5)_2P(O)S(CH_2)_nSC_2H_5$ (series IIIa) and $(C_6H_5)_2P(O)O(CH_2)_nSC_2H_5$ (series IIIb).[15]

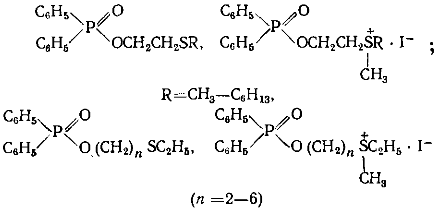
n	$10^{-3}k_a$, litre mole^{-1} min^{-1}	$10^6K_{i,r}$, mole litre^{-1}	$10^6K_{i,S}$, mole litre^{-1}	10^6K_i, mole litre^{-1}
	series IIIa			series IIIb
2	4.2	7.2	7.3	23
3	5.5	3.7	3.2	20
4	5.0	1.5	2.1	14
5	5.2	1.3	1.6	7.4
6	4.8	1.2	0.9	4.8

It follows from the results that the equilibrium constants $K_{i,S}$ and $K_{i,r}$ do indeed characterise the formation of a "non-productive" enzyme–inhibitor complex EIr, different from the Michaelis complex EIn which is rapidly converted into the phosphorylated enzyme EIn'. This has been shown most convincingly by the results of experiments on compounds in series IVa: with increase of n, there is an appreciable increase of the sorbability of the inhibitor, but at the same time the conditions for the formation of the "productive" complex are impaired owing to the increasing incompatibility of the distance between the phosphorus and sulphonium sulphur atoms in the inhibitor molecule and the distance between the esterase and anionic sites of the catalytic centre of the enzyme[15]. The influence of this incompatibility on the irreversible inhibition has been thoroughly investigated for the compounds $CH_3(C_2H_5O)P(O)S(CH_2)_nC_2H_5$ and their methosulphates[16].

Table 5. Constants for the inhibition of BuCE by the compounds $(C_6H_5)_2P(O)S(CH_2)_n\overset{+}{S}(CH_3)C_2H_5.I^-$ (series (IVa) and $(C_6H_5)_2P(O)O(CH_2)_n\overset{+}{S}(CH_3)C_2H_5.I^-$ (series IVb).[15]

n	$10^{-4}k_a$ litre mole^{-1} min^{-1}	$10^7K_{i,r}$, mole litre^{-1}	$10^7K_{i,S}$, mole litre^{-1}	10^6K_i, mole litre^{-1}
	series IVa			series IVb
2	49	10	4 4	13
3	6.0	9.2	3.1	3.0
4	5.3	6.4	2.9	2.0
5	3.0	4.8	2.5	1.6
6	2.5	4.5	1.9	1.2

The observed enhancement of the sorbability of the inhibitors on the active surface of BuCE with increase of the size of the alkyl group attached to the sulphide or sulphonium sulphur in compounds of series Ia and IIa and with increase in the length of the polymethylene chain in compounds of series IIIa and IVa takes place owing to the improvement of the binding of the diphenylphosphinothioates to the esterase site of BuCE. Evidently it is caused by the enhanced interaction of the inhibitor with the enzyme near the anionic site. A characteristic feature is that the changes in $K_{i,S}$ and $K_{i,r}$ are in all cases correlated with the change in the K_i for the corresponding oxygen analogues[13,15]:

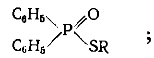


R=CH$_3$—C$_6$H$_{13}$,

(n =2—6)

(series Ib, IIb, IIIb, and IVb, Tables 2–5), which indicates the reliability of the results.

The study of the anticholinesterase activity of diphenylphosphinothioate thioesters[17,18] (series V, Table 6), i.e.



R=$CH_3C_6H_{13}$; iso-C_3H_7, iso-C_4H_9, or iso-C_5H_{11}

showed that these compounds inhibit cholinesterases via the combined mechanism. Both the reversible and irreversible inhibiting activities depend on the length and degree of branching of the alkylthio-group. Thus, when straight-chain alkyl substituents in the alkylthio-groups are displaced by branched substituents, a sharp decrease of both the irreversible and reversible anticholinesterase activities is observed in relation to ACE.[17] In experiments with BuCE [18] such replacement actually increases the inhibiting activity of the compounds (Table 6). Therefore compounds with straight-chain substituents inhibit ACE more strongly [k_a(ACE)/k_a(BuCE) > 1], while compounds with branched substituents inhibit BuCE more strongly [k_a(ACE)/k_a(BuCE) < 1].

Table 6. Constants for the inhibition of cholinesterases by the compounds $(C_6H_5)_2P(O)SR$ (series V).[18]

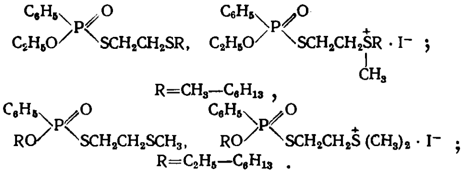
R	$10^{-2}k_a$, litre mole^{-1} min^{-1}	$10^5K_{i,r}$, mole litre^{-1}	$10^5K_{i,S}$, mole litre^{-1}	$10^{-2}k_a$, litre mole min^{-1}	$10^5K_{i,r}$, mole litre^{-1}	$10^6K_{i,S}$, mole litre^{-1}	k_a(ACE)/ k_a(BuCE)
	ACE			BuCE			
CH_3	2.2	7.7	36	1.2	4,3	26	1.8
C_2H_5	4.9	4.6	19	1.5	3,5	14	3.3
C_3H_7	12	1.9	3.2	1.9	3.2	7.6	6.3
C_4H_9	25	0.62	1.3	2.2	1.8	5,0	11.4
C_5H_{11}	46	0.44	0.72	2.4	1.7	4,3	19.2
C_6H_{13}	58	0.29	0.64	2.5	1.4	2,8	23.2
iso-C_3H_7	0.3	50	50	2.9	4.5	16	0.10
iso-C_4H_9	0.5	14	14	8.5	3.7	6.1	0.06
iso-C_5H_{11}	0.7	82	8.2	27	2.2	3.2	0.026

It follows from these results that the enhancement of the hydrophobic sorption of inhibitors on the active surfaces of cholinesterases via the alkylthio-groups increases the anticholinesterase activity of OPI of the types investigated only when the given effect is consistent with the hydrophobic sorption of phenyl groups on the hydrophobic regions located near the esterase site of the enzyme, i.e. when the increase of the activity of the OPI does not impair the "productive" sorption of the inhibitor on the active surface of the enzyme. If the impairment occurs, then, instead of an increase, a decrease of the anticholinesterase activity should take place owing to the "non-productive" sorption, which occurs when ACE interacts with OPI having branched alkylthio-groups[17].

On the whole the result of experiments with diphenylphosphenothioate esters confirm the existing ideas concerning the "productive" and "non-productive" sorption developed to explain the causes of the selective catalytic activity of chymotrypsin[19,20] and cholinesterases[21,22].

III. REACTIONS OF CHOLINESTERASES WITH PHENYLPHOSPHONOTHIOATE, CYCLOHEXYLPHOSPHONOTHIOATE, AND BENZYLPHOSPHONOTHIOATE THIOESTERS

In order to investigate the influence of hydrophobic sorption on the manifestation of combined inhibition by OPI, various phenylphosphonothioate esters were synthesised and their anticholinesterase activity was investigated[23,24]:



These compounds differ from those discussed above by the fact that they contain a straight-chain alkoxy-group at the phosphorus atom instead of the bulky phenyl group (Tables 7 and 8).

Table 7. Constants ($10^{-4}k_{II}$, litre mole^{-1} min^{-1}) for the inhibition of cholinesterases by the compounds $C_6H_5(C_2H_5O)P(O)SCH_2CH_2SR$ (series VI).[25]

R	ACE	BuCE	R	ACE	BuCE
CH_3	6.1	1.3	C_4H_9	23	66
C_2H_5	3.1	3.7	C_5H_{11}	7.1	19
C_3H_7	2.6	1.1	C_6H_{13}	1.7	15

Table 8. Constants ($10^{-7}k_{II}$, litre mole^{-1} min^{-1}) for the inhibition of cholinesterases by the compounds $C_6H_5(C_2H_5O)P(O)SCH_2CH_2\overset{+}{S}(CH_3)R.I^-$ (series VII).[25]

R	ACE	BuCE	R	ACE	BuCE
CH_3	15	0.63	C_4H_9	5.7	7.6
C_2H_5	7.6	1.8	C_5H_{11}	12	6.5
C_3H_7	11	5.4	C_6H_{13}	14	3.7

The replacement of one phenyl group in compounds of series Ia and IIa by an alkoxy-group led to a sharp alteration of the nature of the inhibition of ACE and BuCE. In contrast to the analogous diphenylphosphinothioate esters, *O*-ethyl phenylphosphonothioates of both sulphide (series VI, Table 7) and sulphonium (series VII, Table 8) types cause only the irreversible inhibition of cholinesterases[25]. The $\lg(v_0/v_t)-t$ linear plots for these substances pass through the origin of coordinates. Furthermore, the values of k found are almost independent of the concentration of the inhibitors. The absence of reversible inhibition indicates a complementarity between the compounds and the active centre of the enzyme such that "non-productive" sorption is either completely absent or is so weak that it cannot be recorded with the aid of the methods described.

Thus, when the alkylthio-group, which may be sorbed on the hydrophobic region near the anionic site, became sufficiently elongated, the combined type of inhibition could not be detected either for ACE or for BuCE.

Next an attempt was made to find inhibitors of the combined type among compounds analogous to those discussed above but having alkoxy-groups of different lengths, capable of being sorbed on the hydrophobic regions near the esterase centre. *O*-Alkyl *S*-(β-methylthioethyl) phenylphosphonothioates (series VIII, Table 9) and their methiodides (series IX, Table 10) were selected as compounds of this kind[26]. In experiments with BuCE combined inhibition was observed for compounds with long alkoxy-groups (C_5H_{11}, C_6H_{13}). For compounds with short alkoxy-groups, only irreversible inhibition was observed[26]. In the experiments with ACE the reversible component was shown only for the last two compounds of the sulphide type (series VIII, Table 9). Substances of the sulphonium type (series (IX) showed only irreversible inhibition (Table 10), which permitted the conclusion that in the case of ACE an increase of the tendency of the inhibitor towards hydrophobic sorption on the active surface of the enzyme, both near the anionic and esterase sites, is not accompanied by the formation of a "non-productive" enzyme–inhibitor complex, as in the case of BuCE.[26]

Table 9. Constants for the inhibition of cholinesterases by the compounds $C_6H_5(RO)P(O)SCH_2CH_2SCH_3$ (series VIII).[26]

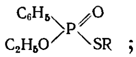
R	10^{-4} k_{II}, litre mole^{-1} min^{-1}	10^6 $K_{i,r}$, mole litre^{-1}	10^6 $K_{i,S}$, mole litre^{-1}	10^{-4} k_{II}, litre mole^{-1} min^{-1}	10^6 $K_{i,r}$, mole litre^{-1}	10^7 $K_{i,S}$, mole litre^{-1}
		ACE			BuCE	
C_2H_5	6.1	—	—	1.3	—	—
C_3H_7	5.5	—	—	7.4	—	—
C_4H_9	15	—	—	26	—	—
C_5H_{11}	17*	4.1	1.3	38	2.1	6.0
C_6H_{13}	19*	2.9	1.5	74	3.0	2.3

*The values of k_a (litre mole^{-1} min^{-1}) are quoted.

Table 10. Constants for the inhibition of cholinesterases by the compounds $C_6H_5(RO)P(O)SCH_2CH_2\overset{+}{S}(CH_3)_2.I^-$ (series IX).[26]

R	10^{-7} k_{II}, litre mole^{-1} min^{-1}	10^{-7} k_{II}, litre mole^{-1} min^{-1}	10^8 $K_{i,r}$, mole litre^{-1}	10^9 $K_{i,S}$, mole litre^{-1}
	ACE		BuCE	
C_2H_5	15	0.63	—	—
C_3H_7	5.5	3.4	—	—
C_4H_9	24	11	—	—
C_5H_{11}	20	2.2	1.9	4.8
C_6H_{13}	12	3.1	4.4	5.9

In the study of the anticholinesterase activity of phenylphosphonothioate thioesters without any polar substituents in the alkylthio-group,



R=CH_3—C_6H_{13} ,

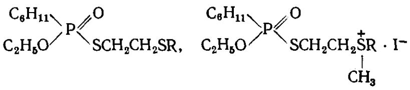
(series X, Table 11) the eliminated part of the CPI molecule was found to influence the nature of the anticholinesterase activity[27]. In contrast to *O*-ethyl *S*-(*β*-alkylthioethyl) phenylphosphonothioates and their methiodides (series VI–IX), all the compounds of this series inhibited ACE and BuCE via the combined mechanism. Evidently the absence from compounds of series X of dipolar and particularly cationic groups in the eliminated part of the molecule impairs the conditions for the correct orientation of the molecule on the active surface of the enzyme, on the one hand, and decreases the electrophilic phosphorylating capacity, on the other, which leads to a distinct combined inhibition of the catalytic activity of cholinesterases.

However, the dipolar and cationic groups in the eliminated part of the OPI molecule are by no means always able to ensure "productive" sorption. This was manifested not only for diphenylphosphinothioate esters, but also for two phenylphosphonothioate esters (Tables 9 and 10). In the first instance the orienting influence of the mercapto-group was interferred with by the two phenyl substituents, and in the second by the phenyl and alkoxy-substituents next to the C_5H_{11} and C_6H_{13} groups. In the presence of smaller alkyl groups concerted sorption of the phosphoryl component and of the mercapto-group was observed and there was no reversible component in the inhibiting activity of the CPI.

Table 11. Constants for the inhibition of cholinesterases by the compounds $C_6H_5(C_2H_5O)P(O)SR$ (series X).[27]

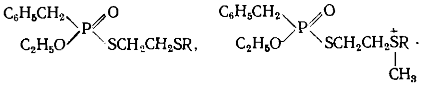
R	10^{-3} k_a, litre mole^{-1} min^{-1}	10^5 $K_{i,r}$, mole litre^{-1}	10^6 $K_{i,S}$, mole litre^{-1}	10^{-3} k_a, litre mole^{-1} min^{-1}	10^5 $K_{i,r}$, mole litre^{-1}	10^5 $K_{i,S}$, mole litre^{-1}
		ACE			BuCE	
CH_3	0.29	76	6.3	1.0	20	5.0
C_2H_5	0.38	11	11	0.14	150	6.1
C_3H_7	0.26	51	15	0.28	29	5.7
C_4H_9	0.58	29	8.0	0.77	12	2.6
C_5H_{11}	1.15	5.7	1.8	4.5	4.5	0.64
C_6H_{13}	2.10	2.2	3.0	51	0.62	0.62

The influence of hydrophobic substituents at the phosphorus atom on the combined inhibition of cholinesterases by OPI was also investigated for a number of cyclohexylphosphonothioate thioesters[28] (series XI and XII, Tables 12 and 13);



R=C_2H_5—C_9H_{19}

and for benzylphosphonothioate thioesters[29] (series XIII and XIV, Tables 14 and 15):



R=C_2H_5—C_9H_{19} .

Table 12. Constants for the inhibition of cholinesterases by the compounds $C_6H_{11}(C_2H_5O)P(O)SCH_2CH_2SR$ (series XI).[30]

R	10^{-2} k_a, litre mole^{-1} min^{-1}	10^6 $K_{i,r}$, mole litre^{-1}	10^5 $K_{i,S}$, mole litre^{-1}	10^{-3} k_a, litre mole^{-1} min^{-1}	10^6 $K_{i,r}$, mole litre^{-1}	10^6 $K_{i,S}$, mole litre^{-1}
		ACE			BuCE	
C_2H_5	1.5	29	9.7	0.65	13	28
C_3H_7	2.8	8.0	4.8	6.3	2.0	17
C_4H_9	4.0	6.0	6.6	25	0.9	1.4
C_5H_{11}	2.9	7.2	3.7	23	1.0	3.1
C_6H_{13}	15	1.0	2.9	48	0.53	2.5
C_7H_{15}	8.3	2.0	6.3	5.7	2.2	7.9
C_8H_{17}	9.5	1.3	1.5	16	0.45	0.73
C_9H_{19}	15	0.3	1.3	5.0	0.29	0.89

It was found that the presence of the cyclohexyl group instead of the phenyl group at the phosphorus atom in the case of compounds of the sulphide type leads to a pronounced combined inhibition of BuCE (Table 12).[30] An analogous effect for BuCE has been observed in the presence of the corresponding benzylphosphonothioate thioesters (Table 14),[31] the latter compounds being more active than derivatives of cyclohexylphosphonothioic acid[30].

Table 13. Constants for the inhibition of cholinesterases by the compounds $C_6H_{11}(C_2H_5O)P(O)SCH_2CH_2\overset{+}{S}(CH_3)R.I^-$ (series XII).[30]

R	10^{-5} k_{II}, litre mole^{-1} min^{-1}	10^{-5} k_a, litre mole^{-1} min^{-1}	10^6 $K_{i,r}$, mole litre^{-1}	10^6 $K_{i,S}$, mole litre^{-1}
	ACE	BuCE		
C_6H_5	1.0	0.57	14	70
C_3H_7	0.7	0.84	5.8	63
C_4H_9	1.1	9.5	0.42	8.4
C_6H_{11}	3.3	16	1.5	12
C_6H_{13}	9.4	12	5.2	25
C_7H_{15}	10	7.8	5.0	20
C_8H_{17}	12	3.9	1.4	11
C_9H_{19}	2.8	2.5	0.85	9

Table 14. Constants for the inhibition of cholinesterases by the compounds $C_6H_5CH_2(C_2H_5O)P(O)SCH_2CH_2SR$ (series XIII).[31]

R	10^{-4} k_a, litre mole^{-1} min^{-1}	10^6 $K_{i,r}$, mole litre^{-1}	10^6 $K_{i,S}$, mole litre^{-1}	10^{-5} k_a, litre mole^{-1} min^{-1}	10^7 $K_{i,r}$, mole litre^{-1}	10^8 $K_{i,S}$, mole litre^{-1}
	ACE			BuCE		
C_2H_5	1.5	25	19	0.74	85	95
C_3H_7	2.6	14	16	7.5	59	69
C_4H_9	2.9	19	12	27	2.5	3.2
C_5H_{11}	1.3	23	21	19	8.9	4.1
C_6H_{13}	3.3	9.8	8.3	18	7.2	5.6
C_7H_{15}	21	1.0	1.9	6.5	9.5	7.0
C_8H_{17}	22	3.6	2.2	22	16	6.5
C_9H_{19}	24	3.2	1.9	13	12	4.9

The interaction of cyclohexylphosphonothioate and benzylphosphonothioate thioesters of the onium type (series XII and XIV, Tables 13 and 15) with BuCE takes place differently. In this case the only inhibitors with a combined type of activity are derivatives of cyclohexylphosphonothioic acid (Table 13).[30] Benzylphosphonothioate thioesters of the onium type cause only the irreversible inhibition of BuCE (Table 14).[31]

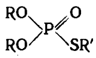
Table 15. Constants (10^{-7} k_{II}, litre mole^{-1} min^{-1}) for the inhibition of cholinesterases by the compounds $C_6H_5CH_2(C_2H_5O)P(O)SCH_2CH_2\overset{+}{S}(CH_3)R.I^-$ (series (XIV).[31]

R	ACE	BuCE	R	ACE	BuCE
C_2H_5	1.0	6,5	C_6H_{13}	0.94	8.2
C_3H_7	0.82	21	C_7H_{15}	1.4	13
C_4H_9	1.2	12	C_8H_{17}	1.6	88
C_5H_{11}	1.3	34	C_9H_{19}	2.8	12

In experiments with ACE only irreversible inhibition was observed in all cases (Tables 13 and 15). These data and also those obtained in the study of the analogous phenylthiophosphonothioate thioesters (series VI–IX) show that the combined inhibition of the catalytic activity of cholinesterases is in most cases promoted by the presence of hydrophobic groups in the inhibitor molecule, particularly those in the phosphorylating component, and is hindered by the presence of polar groups. This is manifested most clearly in the case of ACE.

IV. INTERACTION OF CHOLINESTERASES WITH *OO*-DIALKYL *S*-ALKYL PHOSPHOROTHIOATES

Combined inhibition of cholinesterases does not occur solely when bulky hydrophobic substituents are present at the phosphorus atom. This effect is shown distinctly in those instances where there are two alkoxy-groups at the phosphorus atom. Thus *OO*-dialkyl *S*-alkyl phosphorothioates



$R = C_4H_9$ or C_6H_{13}; $R' = CH_3C_6H_{13}$
iso-C_4H_9, or iso-C_5H_{11},

with two butoxy-[32] and two hexyloxy-groups[33] (series XV and XVI, Tables 16 and 17) cause the combined inhibition of cholinesterase, the reversible component being in all cases more pronounced in the interaction with BuCE than with ACE.

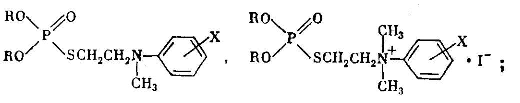
Table 16. Constant for the inhibition of cholinesterases by the compounds $(C_4H_9O)_2P(O)SR$ (series XVI).[32]

R	10^{-4} k_a, litre mole^{-1} min^{-1}	10^5 $K_{i,r}$, mole litre^{-1}	10^6 $K_{i,S}$, mole litre^{-1}	10^{-5} k_a, litre mole^{-1} min^{-1}	10^7 $K_{i,r}$, mole litre^{-1}	10^7 $K_{i,S}$, mole litre^{-1}
	ACE			BuCE		
CH_3	0.75	34	11	0.12	27	11
C_2H_5	1.2	19	31	0.13	16	31
C_3H_7	0.85	31	24	0.86	33	14
C_4H_9	1.2	4.5	9.9	3.2	7.1	5.5
C_5H_{11}	2.1	1.7	4.4	7.7	1.9	1.9
C_6H_{13}	2.2	7.5	3.4	61	0.1	0.26
iso-C_4H_9	2.4	31	4.7	6.2	1.6	1.4
iso-C_5H_{11}	9.4	18	3.7	2.0	16	1.0

Table 17. Constants for the inhibition of cholinesterases by the compounds $(C_6H_{13}O)_2P(O)SR$ (series XVI).[33]

R	10^{-3} k_a, litre mole^{-1} min^{-1}	10^6 $K_{i,r}$, mole litre^{-1}	10^6 $K_{i,S}$, mole litre^{-1}	10^{-5} k_a, litre mole^{-1} min^{-1}	10^7 $K_{i,r}$, mole litre^{-1}	10^7 $K_{i,S}$, mole litre^{-1}
	ACE			BuCE		
CH_3	4.9	43	2.4	4.5	3.9	2.2
C_2H_5	3.3	79	30	1.2	31	0.64
C_3H_7	13	3.7	4.9	3.3	1,7	1.2
C_4H_9	21	1.9	2.6	2,8	6,0	1.1
C_5H_{11}	14	1.9	1.9	1.3	42	2.7
C_6H_{13}	8.1	2.3	2.4	2.1	7.8	4.6
iso-C_4H_9	5.3	5.0	4.2	1.0	40	4.8
iso-C_5H_{11}	15	2.1	1.5	5.9	2.9	1.6

The combined inhibition of the catalytic activity of cholinesterases is apparently fairly characteristic of phosphorothioate thioesters even when there are small alkoxy-groups at the phosphorus atom. This has been shown for a series of *OO*-dialkyl *S*-[β-(*NN*-arylmethylamino)ethyl] phosphorothioates and their methiodides [34,35]:



R=C_3H_7, C_4H_9, iso-C_3H_7; X=H, *n*-, *m*-CH_3; *p*-, *m*-CH_3O, *p*-, *m*-Cl

It was found that OPI of the above type, having straight-chain alkoxy-groups at the phosphorus atom, give rise to combined inhibition [36,37]. This applies both to "uncharged" compounds (series XVII–XIII, Tables 18 and 19) and to compounds of the onium type (series XIX and XX, Tables 20 and 21). In all cases combined inhibition is shown more in relation to BuCE than to ACE.

Table 18. Constants for the inhibition of cholinesterases by the compounds $(C_3H_7O)_2P(O)SCH_2CH_2N(CH_3)C_6H_4R$ (series XVII). [36]

R	10^{-5} k_{II}, litre mole^{-1} min^{-1}	10^7 K_i, S, mole litre^{-1}	10^{-7} k_{II}, litre mole^{-1} min^{-1}	10^8 K_i, S, mole litre^{-1}
	ACE		BuCE	
p-OCH_3	0.9	10.2	0.2	6.8
p-CH_3	1.6	7.6	0.7	2.2
m-CH_3	1.8	5.5	0.8	2.8
H	1.7	8.5	1.6	1.0
m-OCH_3	1.5	7.5	0.9	2.2
p-Cl	4.7	1.7	1.3	1.0
m-Cl	3.1	3.4	2.1	1.2

Table 19. Constants for the inhibition of cholinesterases by the compounds $(C_4H_9O)_2P(O)SCH_2CH_2N(CH_3)C_6H_4R$ (series XVIII). [37]

R	10^{-5} k_{II}, litre mole^{-1} min^{-1}	10^7 K_i, S, mole litre^{-1}	10^{-7} k_{II}, litre mole^{-1} min^{-1}	10^9 K_i, S, mole litre^{-1}
	ACE		BuCE	
p-OCH_3	2.7	2.3	0.6	1.6
p-CH_3	13	1.5	2.5	6.9
m-CH_3	4.7	3.2	2.7	5.7
H	6.8	2.6	2.0	9.0
m-OCH_3	3.2	3.9	4.3	2.1
p-Cl	12	0.9	3.0	3.5
m-Cl	5.4	2.6	2.6	3.7

When there are two branched isopropoxy-groups at the phosphorus atom, combined inhibition is not observed in all cases [38]. Thus the reversible component is observed in the inhibition of ACE and BuCE only by "uncharged" compounds (series XXI, Table 22). The only exception is the *p*-methoxy-derivative, which causes only the irreversible inhibition of BuCE. Only some CPI of the onium type exhibit the combined type of inhibition in relation to ACE, while BuCE is only irreversibly inhibited by these compounds [38] (series XXII, Table 23). Thus BuCE does not always tend to be more readily inhibited via the combined mechanism by *OO*-dialkyl *S*-alkyl phosphorothioate esters, in contrast to the phosphonothioate thioesters.

Table 20. Constants for the inhibition of cholinesterases by the compounds $(C_3H_7O)_2P(O)SCH_2CH_2\overset{+}{N}(CH_3)_2C_6H_4R.I^-$ (series XIX). [36]

R	10^{-7} k_{II}, litre mole^{-1} min^{-1}	10^9 K_i, S, mole litre^{-1}	10^{-8} k_{II}, litre mole^{-1} min^{-1}	10^{10} K_i, S, mole litre^{-1}
	ACE		BuCE	
p-OCH_3	1.5	9.8	2.1	3.3
p-CH_3	3.6	3.3	2.8	1.8
m-CH_3	2.6	5.5	3.1	2.1
H	2.8	3.2	6.4	2.8
m-OCH_3	2.2	18	3.6	1.9

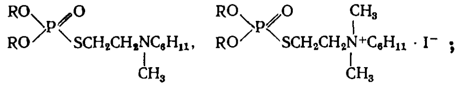
Table 21. Constants for the inhibition of cholinesterases by the compounds $(C_4H_9O)_2P(O)SCH_2CH_2\overset{+}{N}(CH_3)_2C_6H_4R.I^-$ (series XX). [37]

R	10^{-7} k_{II}, litre mole^{-1} min^{-1}	10^9 K_i, S, mole litre^{-1}	10^{-8} k_{II}, litre mole^{-1} min^{-1}	10^{10} K_i, S, mole litre^{-1}
	ACE		BuCE	
p-OCH_3	2.6	4.1	2.6	2.5
p-CH_3	6.1	1.7	3.6	3.6
m-CH_3	3.7	3.2	4.9	2.6
H	6.3	1.9	6.2	7.4
m-OCH_3	4.2	2.6	3.2	2.1

Table 22. Constants for the inhibition of cholinesterases by the compounds (iso-$C_3H_7O)_2P(O)SCH_2CH_2N(CH_3)C_6H_4R$ (series XXI). [38]

R	10^{-8} k_a, litre mole^{-1} min^{-1}	10^6 $K_{i,r}$, mole litre^{-1}	10^6 K_i, S, mole litre^{-1}	10^{-5} k_a, litre mole^{-1} min^{-1}	10^7 $K_{i,r}$, mole litre^{-1}	10^7 K_i, S, mole litre^{-1}
	ACE			BuCE		
p-OCH_3	2.5	77	32	1.0	—	—
p-CH_3	4.3	30	16	4.2	25	4.8
m-CH_3	3.7	32	9.4	2.4	29	10
H	0.9	15	12	2.9	35	7.0
m-OCH_3	3.4	65	28	3.7	34	7.4
p-Cl	43	13	2.6	64	0.18	0.31
m-Cl	45	0.46	2.3	40	5.0	1.0

Analogous results were also obtained in experiments with *OO*-dialkyl *S*-alkyl phosphorothioate esters containing the cyclohexyl group at the nitrogen atom in the β-position relative to the thioester group [39]:



R=C_2H_5, C_3H_7, C_4H_9, or iso-C_3H_7.

Compounds with isopropoxy- or n-butoxy-groups at the phosphorus atom, exhibit the combined type of inhibition only in relation to ACE, the effect being observed with both "uncharged" compounds (series XXIII, Table 24) and with methiodides (series XXIV, Table 25). Organophosphorus inhibitors of the above types cause only the irreversible inhibition of BuCE.

Table 23. Constants for the inhibition of cholinesterases by the compounds $(iso\text{-}C_3H_4O)_2P(O)SCH_2CH_2\overset{+}{N}(CH_3)_2C_6H_4R.I^-$ (series XXII).[38]

R	10^{-5} k_a, litre mole^{-1} min^{-1}	10^7 K_i, r, mole litre^{-1}	10^7 K_i, s, mole litre^{-1}	10^{-7} k_{II}, litre mole^{-1} min^{-1}
	ACE			BuCE
p-OCH_3	12	—	—	2.3
p-CH_3	16	—	—	12
m-CH_3	30	1.4	0.5	8.1
H	9.3	5.5	1.0	5.8
m-OCH_3	29	2.4	62.	13

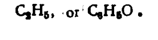
Table 24. Constants for the inhibition of cholinesterases by the compounds $(RO)_2P(O)SCH_2CH_2N(CH_3)C_6H_{11}$ (series XXIII).[39]

R	10^{-5} k_a, litre mole^{-1} min^{-1}	10^8 K_i, r, mole litre^{-1}	10^7 K_i, s, mole litre^{-1}	10^{-7} k_{II}, litre mole^{-1} min^{-1}
	ACE			BuCE
C_2H_5	4.6	—	—	3.2
C_3H_7	24	—	—	42
iso-C_3H_7	0.18	30	51	1.3
C_4H_9	35	0.34	0.19	22

Table 25. Constants for the inhibition of cholinesterases by the compounds $(RO)_2P(O)SCH_2CH_2\overset{+}{N}(CH_3)_2C_6H_{11}.I^-$ (series XXIV).[39]

R	10^{-6} k_a, litre mole^{-1} min^{-1}	10^5 K_i, r, mole litre^{-1}	10^6 K_i, s, mole litre^{-1}	10^{-7} k_{II}, litre mole^{-1} min^{-1}
	ACE			BuCE
C_2H_5	2.0	—	—	6.3
C_3H_7	0.1	—	—	67
iso-C_3H_7	13	1.4	1.1	5.0
C_4H_9	0.13	$3.0 \cdot 10^{-3}$	$6.3 \cdot 10^{-3}$	43

The above experimental data permit the conclusion that the combined inhibition of the catalytic activity of cholinesterases is most effectively promoted by hydrophobic substituents in the phosphorylating component of the OPI molecule. However, there are also instances where substituents in the eliminated component of the OPI molecule exert a decisive influence. This has been demonstrated for the diphenylmethyl esters of various phosphorus(V) thio-acids[40]:



R=CH_3, C_2H_5, C_6H_5, C_2H_5O, or C_6H_5O; R′=C_2H_5O, C_2H_5, or C_6H_5O.

The tendency of these compounds to exhibit the combined type of inhibition in relation to ACE and BuCE is very pronounced even in those cases where there are groups with short hydrophobic substituents at the phosphorus atom. The presence of two phenoxy-groups at the phosphorus atom leads to the loss of ability by OPI to cause the irreversible inhibition of ACE, but BuCE undergoes combined inhibition under these conditions (series XXV, Table 26).

Table 26. Constants for the inhibition of cholinesterases by the compounds $RR'P(O)SCH(C_6H_5)_2$ (series XXV).[40]

R	R′	10^{-4} k_a, litre mole^{-1} min^{-1}	10^8 K_i, r, mole litre^{-1}	10^7 K_i, s, mole litre^{-1}	10^{-4} k_a, litre mole^{-1} min^{-1}	10^8 K_i, r, mole litre^{-1}	10^7 K_i, s, mole litre^{-1}
		ACE			BuCE		
CH_3	C_2H_5O	49.5	0.99	9.2	1.62	6.5	8.3
C_2H_5O	C_2H_5O	18.4	0.74	6.75	9.43	17.7	8.95
C_2H_5	C_2H_5	0.143	100	34	0.052	2.15	78.7
C_6H_5	C_2H_5O	2.18	10.5	18	23	9.78	1.26
C_6H_5O	C_6H_5O	—	—	12	3.96	22.6	773

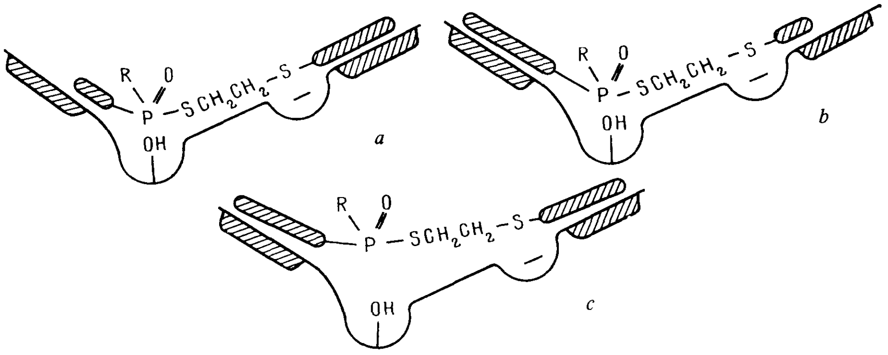
V. CONCLUSION

The results obtained show that BuCE is much more readily inhibited by substances capable of hydrophobic sorption on the active surface of the enzyme than is ACE. This conclusion had been reached earlier[9-11]. In subsequent studies it was clearly confirmed and developed further. In particular, relations were discovered between the structure of OPI with different hydrophobic substituents and their inhibiting activity in relation to ACE and BuCE.[41]

Comparison of the anticholinesterase activities of the diphenylphosphinothioates, phenylphosphonothioates, benzylphosphonothioates, and cyclohexylphosphonothioates presented in this review, as well as the methylphosphonothioates investigated earlier[7] clearly demonstrates differences between the sensitivities of ACE and BuCE to these compounds as a function of the structure of the phosphoryl component in their molecules.

S-Alkylthioethyl compounds with a methyl group at the phosphorus atom exert the strongest irreversible inhibiting activity in relation to ACE. This highly specific enzyme has apparently become adapted to acetylcholine and for this reason interacts faster with substances containing the $CH_3-P=O$ group, which simulates the $CH_3-C=O$ group of acetylcholine. Substances with a phenyl group at the phosphorus atom resemble methylphosphonothioate esters. *S*-Alkylthioethyl esters of phosphonothioic acids with benzyl and particularly cyclohexyl groups at the phosphorus atom inhibit ACE much less.

Thus substances of the type $A(C_2H_5O)P(O)SCH_2CH_2SR$ and $A(C_2H_5O)P(O)SCH_2CH_2\overset{+}{S}(CH_3).I^-$ can be arranged in the following sequence in terms of the irreversible inhibition of ACE as a function of the structure of A: $CH_3 > C_6H_5 > C_6H_5CH_2 > C_6H_{11}$.



Schematic illustration of the "compatible" (*a* and *b*) and "incompatible" (*c*) sorption of OPI on the active surfaces of cholinesterases.

A different type of behaviour is observed when the above compounds act on BuCE—the enzyme which hydrolyses butyrylcholine at the maximum rate and not acetylcholine. Sulphide derivatives of *O*-ethyl alkylphosphonothioates and of diphenylphosphinothioic acid can be arranged in the following sequence in terms of irreversible inhibition: $C_6H_5CH_2(C_2H_5O) > C_6H_5(C_2H_5O) > CH_3(C_2H_5O) > (C_6H_5)_2 > C_6H_{11}(C_2H_5O)$.

Sulphonium derivatives can be arranged in the same sequence in terms of their inhibiting activity subject to an important stipulation with regard to methylphosphonothioate esters: their positions in the series depend on the size of the alkyl group R.

The above series is valid only for $R < C_6H_{13}$. For $R > C_6H_{13}$, the inhibiting activity of methyl derivatives increases and is not inferior to that of benzyl derivatives: $(C_2H_5O)C_6H_5CH_2 \geqslant (C_2H_5O)CH_3 > (C_2H_5O)C_6H_6 > (C_6H_5)_2 > (C_2H_5O)C_6H_{11}$.

Thus in the presence of large substituents, which firmly attach the inhibitor in the vicinity of the anionic site of BuCE as a result of hydrophobic interaction, the methyl or benzyl group A at the phosphorus atom is "better" for productive sorption and subsequent phosphorylation of the enzyme than the phenyl or cyclohexyl group, while in the presence of small substituents the phenyl group A is "better" than the methyl group. The complementarity of the inhibitor molecule to the active surface of the enzyme, which ultimately determines the occurrence of "productive" sorption, in general depends on the compatibility of the ion–ion, ion–dipole, and hydrophobic interactions, as mentioned above. When these interactions are compatible, the sorbed molecule is oriented on the active centre in such a way that the phosphorus atom and the serine hydroxyl of the enzyme are in close proximity and phosphorylation may occur; this is illustrated schematically in the Figure. When the effects are "incompatible", the inhibitor molecule is arranged in such a way that the phosphorus atom and the serine hydroxyl are separated in space, phosphorylation is difficult, and the combined type of inhibition is shown clearly.

For certain structures of the inhibitors, hydrophobic sorption may promote the correct orientation of the inhibitor on the active surface of the enzyme, as a result of which the rate of irreversible inhibition increases. However, for other structures the sorption may interfere with the "correct orientation": for example, in those cases where the inhibitor molecule, fixed at two hydrophobic sites, is arranged in such a way that the phosphorus atom is separated from the serine hydroxyl of the enzyme active centre. Analogous steric hindrance may arise also when certain sulphide and sulphonium derivatives act on the enzyme, whereupon, as a result of the "incompatibility" of the sorption at the anionic site and in the corresponding hydrophobic region, the ester group of the inhibitor is incorrectly oriented relative to the esterase site of the enzyme.

Effects of this kind, which lower the rate constant for irreversible inhibition and cause the appearance of the reversible component, probably exert the most marked influence when the inhibitor molecule contains bulky hydrophobic groups, particularly those linked directly to the phosphorus atom (two phenyl groups, a cyclohexyl group, and a benzyl group).

Effects of this kind were explained previously by the absence of complementarity between the hydrophobic group of the inhibitor and the hydrophobic region located in the immediate vicinity of the esterase site of the enzyme. In the light of new experimental data, a revised treatment of the above effects is now necessary. The "hydrophobic region–esterase site" complementarity rather than with the complementarity to the hydrophobic region itself is relevant.

Thus it has been shown[9-11] that the introduction of hydrophobic groups into the eliminated or non-eliminated component of the inhibitor molecule enhances its irreversible inhibiting activity, particularly in relation to butyrylcholinesterase. On the basis of the data described, one may now claim that the introduction of bulky hydrophobic groups, particularly several such groups, may lead to the opposite effect, owing to the incompatibility of the orientation of the inhibitor molecule with the active surface of the enzyme: instead of an enhancement, a weakening of the anticholinesterase activity and the appearance of the reversible component are observed.

Thus the data described above show that the anticholinesterase activity of compounds and the nature of their inhibiting effect depend on three factors: on the electrophilic phosphorylating capacity of the inhibitor, on its tendency to undergo hydrophobic sorption on the active surface of the enzyme, and on the complementarity of the inhibitor molecule to the "hydrophobic region–esterase centre" system.

One must recall that the difference between productive and non-productive sorption apparently consists solely in the localisation of the inhibitor molecule on the active surface of the enzyme; the vigorous interactions ensuring both types of sorption are virtually identical. Accordingly, the stabilities of the "productive" (EIn) and "non-productive" (EI_r) complexes should be similar. From this point of view, the quantities $K_{i,S}$ and $K_{i,r}$ are of great interest, because they can yield information about the equilibrium constant for the formation of the Michaelis enzyme–inhibitor complex. When the above quantities are analysed, the most striking fact is that in the vast majority of instances the quantities $K_{i,S}$ and $K_{i,r}$ for BuCE are significantly smaller than for ACE. This was shown particularly clearly in experiments with *S*-alkyl diphenylphosphinothioates[18], *O*-ethyl *S*-alkyl phenylphosphonothioates[27], and *OO*-dibutyl *S*-alkyl phosphorothioates[32], in the sorption of which the hydrophobic interaction plays an extremely significant role. The hydrophobic interaction is known to be more characteristic of BuCE than of ACE. Hence it becomes understandable why BuCE forms more stable complexes than ACE on interaction with the compounds investigated. This applies to both "non-productive" and "productive" complexes.

Attention must be drawn to the fact that frequently there are differences between the quantities $K_{i,S}$ and $K_{i,r}$, characterising the reversible component of the inhibition of cholinesterases. In most instances $K_{i,S}$ is smaller almost by an order of magnitude than $K_{i,r}$, i.e. the inhibiting effect of certain compounds in the hydrolysis of acetylcholine is manifested to a greater extent than in the phosphorylation of the enzyme.

One of the possible causes of this divergence is that the reversible inhibition of the enzymatic hydrolysis of acetylcholine may be associated with the interaction of the OPI, for example via the anionic site, not only with the free enzyme but also with the acetylated enzyme. This hinders deacetylation and thereby reduces the rate of the enzymatic hydrolysis of acetylcholine and therefore affects $K_{i,S}$.[42] Such reversible interaction of the OPI with the phosphorylated enzyme cannot influence $K_{i,r}$, because the phosphorylated enzyme is the final product of the process investigated.

The second cause may be associated with the presence of the "productive" enzyme–inhibitor complex EIn in the reaction medium when the rate of the enzymatic hydrolysis of AX is determined, because there are insufficient grounds for the belief that, following the addition of AX to the reaction mixture of the enzyme and the OPI, the complex EIn is fully dissociated into the inhibitor and the enzyme, which then catalyses the hydrolysis of AX. Even under conditions where the concentration of AX is many times greater that of the OPI, part of the enzyme may be present in the form of the complex EIn if the latter is very stable. Within the narrow inhibitor concentration ranges employed in experiments, the dependence of the rate constant k for the irreversible inhibition on [In] can therefore be either comparatively weak or may not exist at all. In the latter case it is altogether impossible to determine $K_{i,r}$.

It is noteworthy that, in view of the presence of two stages in the phosphorylation process, k should depend on the incubation time t of the enzyme with the inhibitor and on the inhibitor concentration [In] even in the absence of "non-productive" sorption, provided that these parameters vary within wide limits. Methods for the calculation of the rate constants of the individual stages of the process via mechanism (1) are based on the determination of the dependence of k on t and [In].[43,44]

Thus the combined inhibition of cholinesterases by certain organophosphorus inhibitors, which is manifested clearly in experiments and about the occurrence of which there is no doubt, may be caused not only by the "non-productive" sorption of the inhibitor on the enzyme but also by the presence of an enzyme–inhibitor complex in the enzymatic hydrolysis of the substrate.

Evidently, at the level of the modern experimental technique for the investigation of the interaction of cholinesterases with OPI, where there is as yet no possibility of distinguishing experimentally the "productive" and "non-productive" enzyme–inhibitor complexes, the reversible component must be regarded as a result of the binding of the enzyme both in the complex EI_r and in the Michaelis complex EIn.

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The Imide-Amide and Imide-Imide Rearrangements of Imidophosphorus Compounds

V.A.Gilyarov

Data on the imide-amide and imide-imide rearrangements of imidophosphorous compounds are surveyed, the factors influencing the ease of these rearrangements are noted, and information about their mechanisms is given.
The bibliography includes 83 references.

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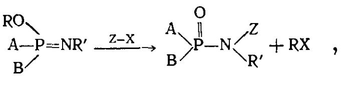
I. INTRODUCTION

Imidophosphorus compounds (IPC) containing at least one alkoxy-group at the phosphorous atom are as a rule converted into the corresponding amides on treatment with electrophiles. This reaction was observed in 1955 by Kabachnik and Gilyarov[1] and called the "imide-amide rearrangement". The centre of electrophilic attack in IPC may be not only the nitrogen atom (as in the imide-amide rearrangement) but also other atoms forming part of the conjugated system, for example, the oxygen atom of the carbonyl group in acetylimidophosphate[2] or the oxygen atom of the phosphoryl group in phosphorylimidophosphates[3], as well as the sulphur atom of thiophosphorylimidophosphates[4]. These reactions have been called the "imide-imide rearrangement"[5]. It is noteworthy that the majority of studies on the imide-amide and imide-imide rearrangements have been carried out during the last ten years.

The IPC nomenclature recommended by IUPAC[6] is used in this review, but in a number of instances, the names of compounds are quoted as given by the authors of the studies under consideration.

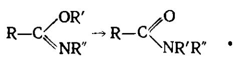
II. THE IMIDE-AMIDE REARRANGEMENT

In a general form the imide-amide rearrangement can be represented schematically as follows[7]:

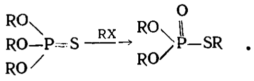


where Z-X is an electrophile and A and B are substituents at the phosphorus atom. Alkyl halides, acyl halides, phosphorus acid chlorides, chlorotrimethylsilane, or the IPC itself (in thermal isomerisation) may be used as the electrophiles. Dealkylation reactions during hydrolysis and on treatment with acids also belong to imide-amide rearrangements.

The imide-amide rearrangement of IPC may be compared with the rearrangement of alkyl imidocarboxylate esters to the corresponding amides[8]:



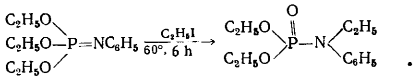
The analogy between the imide-amide rearrangement and the Pishchimuka rearrangement[9] should also be noted:



This analogy is not merely formal, being manifested also by the conditions of the rearrangement and the factors which influence its rate.

1. Rearrangement Under the Influence of Alkylating and Acylating Agents

(a) Rearrangement under the influence of alkyl halides. The first example of the imide-amide rearrangement was described by Kabachnik and Gilyarov[1] in relation to the transformation of triethyl phenylimidophosphate (I) into *O,O*-diethyl-*N*-ethylanilidophosphate (II):



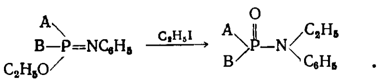
(I) (II)

A study of the reaction of trimethyl arylimidophosphates (III) on refluxing with methyl iodide showed[10,11] that electron-accepting substituents in the benzene ring hinder the isomerisation:

$$\underset{\text{(III)}}{(CH_3O)_3\,P{=}NC_6H_4X} \xrightarrow{CH_3I} \underset{\text{(IV)}}{(CH_3O)_2\,P\,(O)\,N\,(CH_3)\,C_6H_4X}\ .$$

The influence of alkyl halides on the rate of rearrangement of the imidophosphate (I) has been followed in relation to benzyl chloride and ethyl iodide. In the former case the rearrangement proceeds under more severe conditions (heating for 5 h at 130°C) than in the latter (refluxing for 6 h). Thus the same behaviour is observed as in the Pishchimuka thione-thiol rearrangement[12].

A number of workers[11,13,14] studied in detail the influence of substituents A and B in ethoxy(phenylimido)phosphorus compounds (V), having investigated the kinetics of their reactions with ethyl iodide in acetonitrile at 50°C:



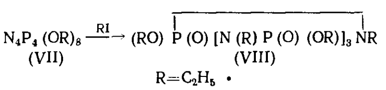
(V) (VI)

It was found that the kinetics are described satisfactorily by a pseudo-first order equation. The rate constants are given in the Table.

The rate constants for the rearrangement of phosphorus(V) acid phenylimides $AB(C_2H_5O)P{=}NC_6H_5$ under the influence of ethyl iodide.

A	B	10^3k, litre mole^{-1} min^{-1}	A	B	10^3k, litre mole^{-1} min^{-1}
C_2H_5O	C_2H_5O	0.92	C_2H_5	C_2H_5O	3.06
C_6H_5	C_2H_5O	1.14	C_2H_5	C_6H_5	4.13
CH_3	C_2H_5O	2.85	C_2H_5	C_2H_5	10.45

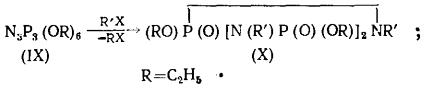
It has been established[15] that the rearrangement of triphosphatriazines and tetraphosphatetrazines is catalysed by alkyl halides. Thus tetraphosphatetrazine (VII) is converted into 2,4,6,8-tetraethoxy-1,3,5,7-tetraethyl-2,4,6,8-tetraphospha-1,3,5,7-tetrazine(VIII) on heating with ethyl iodide (4.7 h, 170°C):



$$\underset{(VII)}{N_4P_4(OR)_8} \xrightarrow{RI} \underset{(VIII)}{(RO)P(O)[N(R)P(O)(OR)]_3NR} ;$$

$R{=}C_2H_5$.

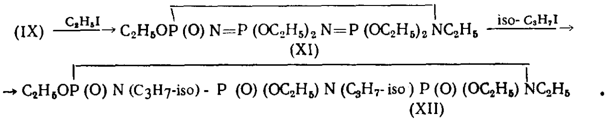
When alkyl halides were used with an alkyl group different to that in the initial triphosphatriazine (IX), compound (X), containing different substituents at the phosphorus and nitrogen atoms, was obtained[16]:



$$\underset{(IX)}{N_3P_3(OR)_6} \xrightarrow[-RX]{R'X} \underset{(X)}{(RO)P(O)[N(R')P(O)(OR)]_2NR'} ;$$

$R{=}C_2H_5$.

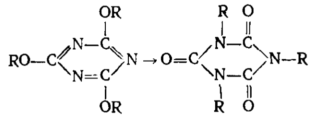
When triphosphatriazine (IX) was refluxed with ethyl iodide in the dark for a week, it was possible to obtain the partial rearrangement product (XI), which, on further heating with isopropyl iodide (35 min, 175–180°C), was converted into 1,3-di-isopropyl-2,4,6-triethoxy-5-ethyl-2,4,6-triphospha-1,3,5-triazine (XII):



$$(IX) \xrightarrow{C_2H_5I} \underset{(XI)}{C_2H_5OP(O)N{=}P(OC_2H_5)_2N{=}P(OC_2H_5)_2NC_2H_5} \xrightarrow{iso\text{-}C_3H_7I}$$

$$\rightarrow \underset{(XII)}{C_2H_5OP(O)N(C_3H_7\text{-}iso)\text{-}P(O)(OC_2H_5)N(C_3H_7\text{-}iso)P(O)(OC_2H_5)NC_2H_5} .$$

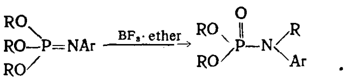
It is noteworthy that a similar rearrangement of alkyl cyanurates has been observed. Under the influence of electrophiles or on heating (180–210°C), 2,4,6-trialkoxy-1,3,5-triazines are converted into 1,3,5-trialkyl-2,4,6-trioxo-1,3,5-triazines[17] (XIII):



(XIII)

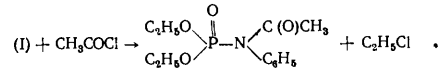
The synthesis of (IV) and (VI) via the imide–amide rearrangement is of preparative value[10,11,13]. A number of chromatographically pure N-methylanilines have been synthesised by the hydrolysis of dimethyl N-methylanilidophosphates.

(b) Rearrangement in the presence of catalytic amounts of boron trifluoride etherate. It was found[18] that the imide–amide rearrangement of arylimidophosphorus compounds takes place under mild conditions (at room temperature or on slight heating) in the presence of catalytic amounts of boron trifluoride etherate:



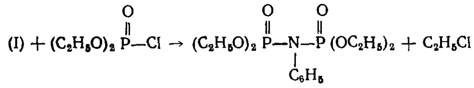
$$(RO)_3P{=}NAr \xrightarrow{BF_3\cdot ether} (RO)_2P(O)N(R)Ar .$$

(c) Rearrangement under the influence of acyl halides, phosphorus acid chlorides, and chlorotrimethylsilane. The reactions of IPC with acylating agents take place much more vigorously than with alkyl halides. Triethyl phenylimidophosphate (I) gives rise to diethyl N-acetylanilidophosphate as a result of an exothermic reaction in iso-octane[1]:



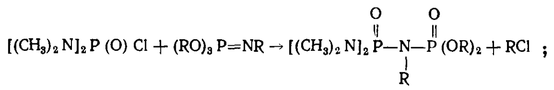
$$(I) + CH_3COCl \rightarrow (C_2H_5O)_2P(O)N(C(O)CH_3)C_6H_5 + C_2H_5Cl .$$

The reactions of dialkyl chlorophosphates and diphenyl chlorophosphinate with phenylimido- and methylimidophosphorus compounds take place vigorously, the corresponding bisphosphoryl compounds being formed[19,20], for example:



$$(I) + (C_2H_5O)_2P(O){-}Cl \rightarrow (C_2H_5O)_2P(O){-}N(C_6H_5){-}P(O)(OC_2H_5)_2 + C_2H_5Cl .$$

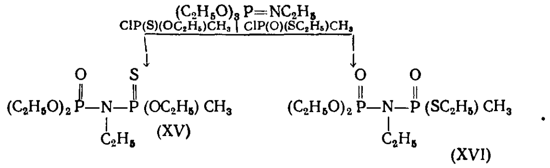
Compounds (XIV) have been synthesised similarly from tetramethyldiamidochlorophosphate[21]:



$$[(CH_3)_2N]_2P(O)Cl + (RO)_3P{=}NR \rightarrow \underset{(XIV)}{[(CH_3)_2N]_2P(O){-}N(R){-}P(O)(OR)_2} + RCl ;$$

$R{=}CH_3$ or C_2H_5 .

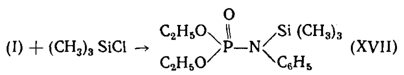
The reaction of O-ethyl methylchlorothiophsophonate and S-ethyl methylchlorothiophosphonate with triethyl ethylimidophosphate leads to the formation of compounds (XV) and (XVI)[22]:



$$(C_2H_5O)_3P{=}NC_2H_5 \text{ with } ClP(S)(OC_2H_5)CH_3 \rightarrow \underset{(XV)}{(C_2H_5O)_2P(O){-}N(C_2H_5){-}P(S)(OC_2H_5)CH_3}$$

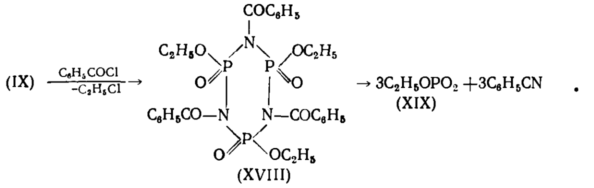
$$(C_2H_5O)_3P{=}NC_2H_5 \text{ with } ClP(O)(SC_2H_5)CH_3 \rightarrow \underset{(XVI)}{(C_2H_5O)_2P(O){-}N(C_2H_5){-}P(O)(SC_2H_5)CH_3} .$$

Thus, in all the reactions of IPC with phosphorus acid chlorides considered phosphorylation takes place at the imide nitrogen atom. This reaction has been suggested as a general method of synthesis of bisphosphoryl-N-aryl(or alkyl)imides and (phosphoryl)(thiophosphoryl)-N-aryl(or alkyl)imides. Thus bis(diphenylphosphoryl)-N-phenylimide, obtained by the method discussed, could not be synthesised by any other procedure[23]. N-Trimethylsilyl derivatives of phosphoric acid amides have been obtained by the reaction of phenylimidophosphorus compounds with chlorotrimethylsilane (4 h, 50°C), for example compound (XVII):



$$(I) + (CH_3)_3SiCl \rightarrow (C_2H_5O)_2P(O)N(Si(CH_3)_3)C_6H_5 \quad (XVII) .$$

The reactions of benzoyl chloride with 2,2,4,4,6,6-hexaethoxy-2,4,6-triphospha-1,3,5-triazine (IX) (1 h, 130–140°C) and 2,2,4,4,6,6,8,8-octaethoxy-2,4,6,8-tetraphospha-1,3,5,7-tetrazine (5 h, 140–150°C) have been investigated[15,24,25]. A mixture of products is obtained in both cases (ethyl chloride, ethyl metaphosphate, and benzonitrile). The authors suggest that the first stage of the reaction is an imide–amide rearrangement as a result of nucleophilic attack by the nitrogen atom on the carbon atom of the carbonyl group; this results in the formation of ethyl chloride and the unstable 1,3,5-tribenzoyl-2,4,6-triethoxy-2,4,6-triphospha-1,3,5-triazine (XVIII):



The intermediate (XVIII) forms on decomposition ethyl metaphosphate (XIX) and benzonitrile. Part of the latter is converted into 2,4,6-triphenyl-1,3,5-triazine under the reaction conditions.

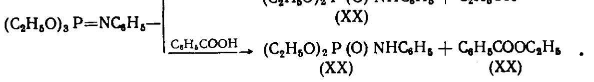
2. Rearrangement During Hydrolysis and on Treatment with Acids

When IPC with at least one alkoxy-group at the phosphorus atom are hydrolysed or treated with acids, they are dealkylated and the imidophosphates is converted into the amidophosphate, i.e. an imide–amide rearrangement takes place. Extensive experimental data on the hydrolysis of IPC have been surveyed in a monograph[26].

The general characteristics are in this case the same as on treatment with other electrophiles, namely the resistance to hydrolysis on treatment with acids increases with enhancement of the electron-accepting properties of the substituent at the nitrogen atom. Thus triethyl methylimidophosphate is readily hydrolysed by atmospheric moisture and on mixing with water heat is evolved[27]:

$$(C_2H_5O)_3\,P{=}NCH_3 \xrightarrow{H_2O} (C_2H_5O)_2\,P\,(O)\,NHCH_3 + C_2H_5OH \ .$$

The imidophosphate (I) is converted into diethyl anilidophosphate (XX) on treatment with benzoic acid in xylene at room temperature[1]:



$$(C_2H_5O)_3\,P{=}NC_6H_5 \begin{cases} \xrightarrow{H_2O} (C_2H_5O)_2\,P\,(O)\,NHC_6H_5 + C_2H_5OH \\ \qquad\qquad\quad (XX) \\ \xrightarrow{C_6H_5COOH} (C_2H_5O)_2\,P\,(O)\,NHC_6H_5 + C_6H_5COOC_2H_5 \ . \\ \qquad\qquad\quad (XX) \qquad\qquad\qquad (XX) \end{cases}$$

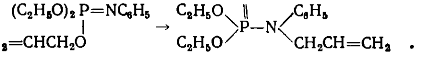
Triethyl diethoxyphosphorylimidophosphate is resistant to the action of formic or acetic acid on heating[27]. It has been found that the interaction of imidophosphates with dry hydrogen chloride is the best method for converting imidophosphates $(RO)_3P{=}NR'$ into amidophosphates $(RO_2)P(O)NHR'$, where R′ is an aryl[1,29], acetyl[30], halogenoacetyl[30], methanesulphonyl[28], dialkoxyphosphoryl, or dialkoxythiophosphoryl[31] group, for example[30]:

$$(C_2H_5O)_3\,P{=}NCOCF_3 \xrightarrow{HCl} (C_2H_5O)_2\,P\,(O)\,NHCOCF_3 + C_2H_5Cl \ .$$

3. Rearrangement on Heating (Thermal Isomerisation)

The greatest number of studies on the imide–amide rearrangement have been devoted to the thermal isomerisation of IPC. Such isomerisation was observed for the first time by Kabachnik and Gilyarov for trimethyl phenylimidophosphate[1]. On being vacuum distilled (at 150–180°, 0.1 mmHg), this substance partly isomerised to dimethyl *N*-methylanilidophosphate. It is of interest to compare this reaction with the thermal isomerisation of trimethyl thionophosphate and trimethyl thiolophosphate[32]. We shall consider the factors influencing the ease of the thermal isomerisation of IPC of the type (RO)ABP=NX; these are as follows: (a) the structure of R in the alkoxy-group; (b) the nature of the sudstituents A and B at the phosphorus atom and of the substituent X at the nitrogen atom.

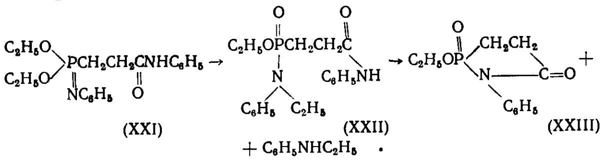
The isomerisation proceeds most readily with methyl esters and is hindered as R increases in size. It has been shown[33] that thermal isomerisation of allyl diethyl phenylimidophosphate takes place at 160°C and the allyl group is the alkylating species:



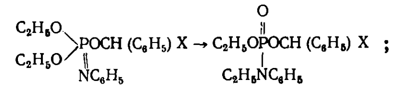
$$\underset{CH_2{=}CHCH_2O}{(C_2H_5O)_2\,\overset{|}{P}{=}NC_6H_5} \rightarrow (C_2H_5O)_2\overset{O}{\overset{\|}{P}}{-}N\begin{smallmatrix} C_6H_5 \\ CH_2CH{=}CH_2 \end{smallmatrix} \ .$$

It is of interest to note that the replacement of the ethoxy-groups at the phosphorus atom by the more electron-accepting phenoxy-groups facilitates isomerisation, which takes place even on distillation (90–120°C).[34]

Pudovik and coworkers described a number of instances of the imide–amide rearrangement. When an attempt was made to distill the imidophosphonate (XXI), the cyclic phosphonate (XXIII) was obtained[35], evidently owing to cyclisation of the product (XXII) of the imide–amide rearrangement formed initially:



The thermal isomerisation of the imidophosphates (XXIV)[36] and (XXV)[37] leads to the corresponding *N*-ethylanilidophosphates:



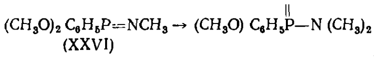
$$(C_2H_5O)_2\underset{NC_6H_5}{\overset{}{\underset{\|}{P}}}OCH\,(C_6H_5)\,X \rightarrow C_2H_5O\overset{O}{\overset{\|}{\underset{C_2H_5NC_6H_5}{\underset{|}{P}}}}OCH\,(C_6H_5)\,X \ ;$$

(XXIV) : X=COOR;
(XXV) : X=P (O) (OC₂H₅)₂.

It is noteworthy that the ethoxy-group is then involved in the isomerisation (when the phenyl group is present at the nitrogen atom)[35-37].

When an attempt was made to obtain trialkyl imidophosphates unsubstituted at the nitrogen atom by the interaction of trialkyl phosphites with hydrazoic acid, their thermal isomerisation products were isolated: *O,O*-dialkyl *N*-alkylamidophosphates[38,39].

When a methyl or ethyl group is present at the nitrogen atom, heat is required for the rearrangement[40]. Thus trimethyl methylimidophosphate and *O,O*-dimethyl phenyl(methylimido)phosphonate (XXVI) isomerised to the corresponding amides in 1.5 h at 120°C:

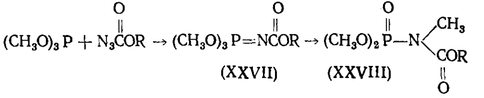


$$\underset{(XXVI)}{(CH_3O)_2\,C_6H_5P{=}NCH_3} \rightarrow (CH_3O)\,C_6H_5\overset{O}{\overset{\|}{P}}{-}N\,(CH_3)_2 \ .$$

It was not possible to isolate the thermal isomerisation products of ethylimidophosphorus compounds[40]. The thermal isomerisation of trimethyl methylimidophosphate has been mentioned[41], but without a description of the experiment.

A considerable number of studies have been devoted to the thermal isomerisation of IPC containing electron-accepting substituents at the nitrogen atom—such as alkoxycarbonyl (ROCO), arenesulphonyl ($ArSO_2$), disubstituted phosphoryl [XYP(O)], dialkoxythiophosphoryl [$(RO_2)P(S)$], etc. groups.

Trimethyl alkoxycarbonylimidophosphates (**XXVII**) isomerise at the boiling point of ether[42]:

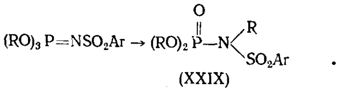


$$(CH_3O)_3P + N_3\overset{O}{\overset{\|}{C}}OR \rightarrow (CH_3O)_3P{=}N\overset{O}{\overset{\|}{C}}OR \rightarrow (CH_3O)_2\overset{O}{\overset{\|}{P}}{-}N{<}^{CH_3}_{\underset{\overset{\|}{O}}{COR}} .$$

(XXVII) (XXVIII)

This results in the formation of the corresponding dimethyl *N*-alkoxycarbonylmethylamidophosphates (**XXVIII**). The replacement of the methoxy-group at the phosphorus atom in compound (**XXVII**) by electron-donating substituents (a methyl group[43] or a dimethylamino-group[44]) increases the resistance to thermal isomerisation; the corresponding compounds may be vacuum distilled without decomposition.

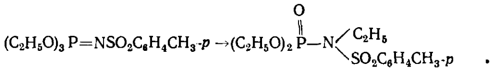
It has been shown[45] that trialkyl arenesulphonylimidophosphates isomerise on heating to esters of *N*-arenesulphonyl-*N*-arylamidophosphoric acids (**XXIX**):



$$(RO)_3P{=}NSO_2Ar \rightarrow (RO)_2\overset{O}{\overset{\|}{P}}{-}N{<}^{R}_{SO_2Ar} .$$

(XXIX)

The isomerisation of triethyl toluene-*p*-sulphonylimidophosphate (**XXX**) to diethyl *N*-toluene-*p*-sulphonyl-*N*-ethylamidophosphate (**XXXI**) during distillation (at 200°C) has been observed[46]:

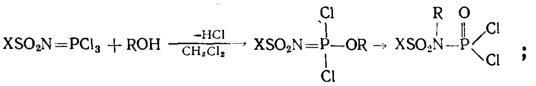


$$(C_2H_5O)_3P{=}NSO_2C_6H_4CH_3\text{-}p \rightarrow (C_2H_5O)_2\overset{O}{\overset{\|}{P}}{-}N{<}^{C_2H_5}_{SO_2C_6H_4CH_3\text{-}p} .$$

(XXX) (XXXI)

According to the authors[46], (**XXXI**) is partly converted into the initial imidophosphate (**XXX**) at 200°C, i.e. the reversible reaction (**XXX**) ⇌ (**XXXI**) takes place. However, the evidence which they present (changes in the ^1H NMR spectrum) is insufficient to sustain this claim.

The imide–amide rearrangement of *O*-alkyl dichloro-(halogenosulphonylimido)-phosphates (**XXXII**) to amidophosphates (**XXXIII**) under the influence of ether or dioxan has been observed[47,48]:

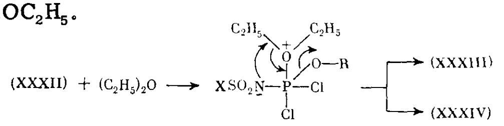


$$XSO_2N{=}PCl_3 + ROH \xrightarrow[CH_2Cl_2]{-HCl} XSO_2N{=}\underset{Cl}{\overset{Cl}{P}}{-}OR \rightarrow XSO_2\overset{R}{N}{-}\overset{O}{\overset{\|}{P}}{<}^{Cl}_{Cl} ;$$

(XXXII) (XXXIII)

$R{=}CH_3$, C_2H_5, or iso- C_3H_7, $X{=}Cl$, or F .

The imidophosphates (**XXXII**) cannot be vacuum distilled (decomposition) and, on refluxing them in ether (or dioxan) for 20 min, compounds (**XXXIII**) were obtained in high yields. Together with the main product (**XXXIII**), the catalytic isomerisation results in the formation of the *N*-ethylamide $XSO_2N(C_2H_5)P(O)Cl_2$ (**XXXIV**) and the mixed ether ROC_2H_5.



The authors[49] observed that, when *NN*-bis(alkoxydichlorophosphoranylidene)-sulphamides (**XXXV**) isomerise, the alkyl group also migrates to the nitrogen atom with formation of the amidophosphates (**XXXVI**):

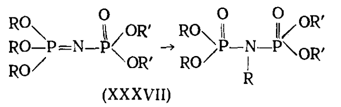
$$O_2S\,(N{=}PCl_2OR)_2 \rightarrow O_2S\,[N\,(R)\,P\,(O)\,Cl_2]_2 .$$

(XXXV) (XXXVI)

The authors[49] noted that ether influences the rate of isomerisation. The phenyl ester (**XXXV**, $R = C_6H_5$) does not isomerise even on prolonged heating.

The mode of thermal isomerisation of phosphorylimidophosphates $(RO)_3P{=}NP(O)XY$ depends on the nature of the substituents at the phosphorus atom (X and Y). When X and Y are alkoxy-groups, the alkyl group migrates exclusively to the imide nitrogen atom. When X and Y are electron-donating (alkyl) groups, the oxygen atom of the phosphoryl group is alkylated (imide–imide rearrangement). If X is an alkyl and Y an alkoxy-group, there is a possibility of the formation of products of both imide–amide and imide–imide rearrangements.

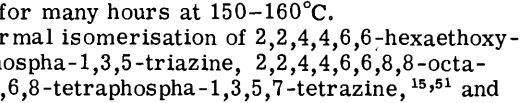
The rate of thermal isomerisation of trialkyldialkoxyphosphorylimidophosphates (**XXXVII**) depends markedly on the nature of the alkyl substituent R[50]:



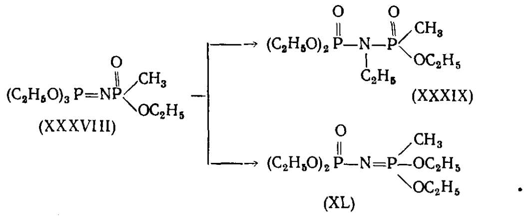
(XXXVII)

Thus trimethyl dimethoxyphosphorylimidophosphate $(CH_3O)_3P{=}NP(O)(OCH_3)_2$ partly isomerises at 50–60°C, and on vacuum distillation (100°C) the isomerisation goes to completion; triethyl dimethoxyphosphorylimidophosphate $(C_2H_5O)_3P{=}NP(O)(OCH_3)_2$ isomerises only as a result of heating for many hours at 150–160°C.

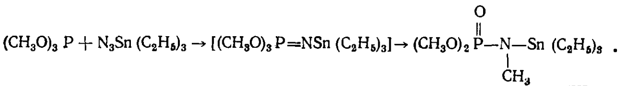
The thermal isomerisation of 2,2,4,4,6,6-hexaethoxy-2,4,6-triphospha-1,3,5-triazine, 2,2,4,4,6,6,8,8-octaethoxy-2,4,6,8-tetraphospha-1,3,5,7-tetrazine,[15,51] and 2,2,4,4,6,6,8,8-octa-(β-chloroethoxy)-2,4,6,8-tetraphospha-1,3,5,7-tetrazine (refluxing for 16 h in dichloroethane)[52] also leads to *N*-alkyl derivatives:



Two products are formed from triethyl ethoxymethylphosphorylimidophosphate (**XXXVIII**): the product of the imide–amide rearrangement (**XXXIX**) under more severe conditions (at 170°C) and the product of the imide–imide rearrangement (**XL**) under milder conditions (at 130°C)[53,54]:



The imide–imide rearrangement of compounds containing other substituents at the nitrogen atom has been little investigated. The reaction of triethylstannyl azide with trimethyl phosphite (heating, 160°C) gave the thermal isomerisation product (**XLI**)[55]:

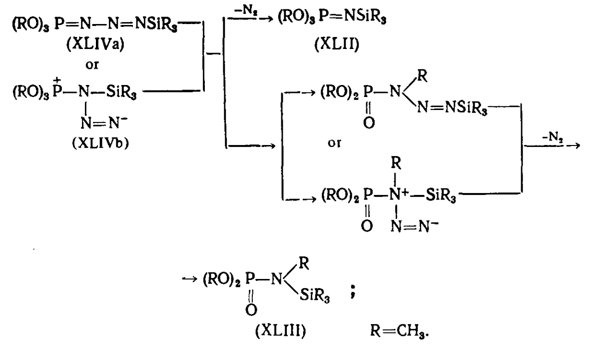


$$(CH_3O)_3P + N_3Sn\,(C_2H_5)_3 \rightarrow [(CH_3O)_3P{=}NSn\,(C_2H_5)_3] \rightarrow (CH_3O)_2\overset{O}{\overset{\|}{P}}{-}\underset{CH_3}{N}{-}Sn\,(C_2H_5)_3 .$$

(XLI)

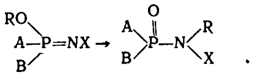
When trimethyl phosphite interacts with trimethylsilyl azide (8 h, 100–120°C), dimethyl *N*-methyl-*N*-trimethylsilylamidophosphate (**XLIII**) is formed together with trimethyl trimethylsilylimidophosphate (**XLII**).[56] Since the imidophosphate (**XLII**) is stable on heating (4 h, 190–200°C), the authors[56] suggested that the intermediate of Staudinger's reaction (cf. Ref. 57), namely the triazene

(XLIVa) or the betaine (XLIVb), undergoes the imide–amide rearrangement:

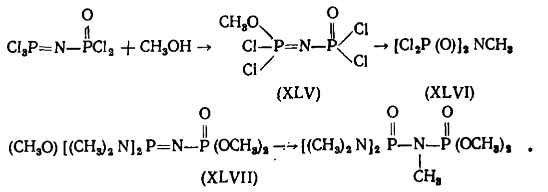


It has been shown recently[58] that, when the imidophosphate $(CF_3CH_2O)_3P{=}NSi(CH_3)_3$ is heated to 200°C, the imide–amide rearrangement does not occur and the linear polymeric product $[-N{=}P(OCH_2CF_3)_2-]_n$ is formed.

Examination of studies on the imide–amide rearrangement on heating permits a conclusion concerning the influence of the substituents at the phosphorus and nitrogen atoms on the rate of isomerisation:



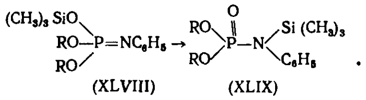
Since the IPC itself plays the role of the alkylating agent in thermal isomerisation, enhancement of the electron-accepting properties of substituents A and B facilitates the isomerisation. Thus *O*-methyl dichloro(dichlorophosphorylimido)phosphate (XLV) partly isomerises to bis(dichlorophosphoryl)-*N*-methylimide (XLVI)[59] even at room temperature. On the other hand, *O*-methyl *N*,*N*,*N'*,*N'*-tetramethyldiamido(dimethoxyphosphorylimido)phosphate (XLVII) remains unchanged after heating for 10 h at 95–100°C, decomposing under more severe conditions (5 h, 130°C)[21]:



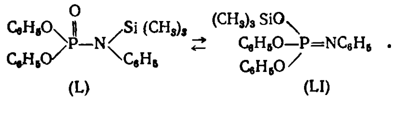
When electron-accepting substituents {arenesulphonyl ($ArSO_2$), dialkoxyphosphoryl [$(RO)_2P(O)$], and similar groups} are introduced at the nitrogen atom, the alkylation capacity of the IPC increases sharply and the thermal isomerisation is facilitated despite the fact that the electron-accepting substituents at the nitrogen atom make the IPC much less nucleophilic. The alkylating capacity of IPC with powerful electron-accepting substituents at the nitrogen atom is greatly superior to that of the corresponding phosphates and thiophosphates[4,7,10].

4. Rearrangement with Participation of the Trimethylsilyl Group

In the examples considered hitherto, the imide–amide rearrangement was irreversible with the exception of the rearrangement of compound (XXXI),[46] which we believe requires confirmation. Instances of both irreversible and reversible migration of the trimethylsilyl group in the $(CH_3)_3Si{-}O{-}P{=}N{-}$ system have been discovered in recent years. The irreversible migration has been found in phosphazines[60]. It has been shown that phosphazines, formed as intermediates in the reaction of dialkyl trimethylsilyl phosphites with methyl diazoacetate, isomerise completely to the corresponding dialkyl *N*-methoxycarbonylmethylene-*N'*-trimethylsilylhydrazidophosphates $(RO)_2P(O)N[Si(CH_3)_3]N{=}CHCOOCH_3$ even at room temperature. Dialkyl trimethylsilyl phenylimidophosphates (XLVIII), formed in the reaction of dialkyltrimethylsilyl phosphites with phenyl azide, are converted under the reaction conditions into dialkyl *N*-phenyl-*N*-trimethylsilylamidophosphates (XLIX).[61,62]



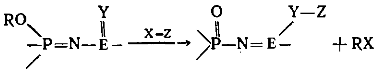
The reversible migration of the trimethylsilyl group in the $O{-}\overset{|}{\underset{|}{P}}{=}N{-}$system has been observed for compound (XLIX, R = CH_3) (on heating) and for diphenyl *N*-phenyl-*N*-trimethylsilylamidophosphate (L).[63] In the latter case the product contains 89% of (L) and 11% of form (LI) at 28°C:



At 129°C the contents of forms (L) and (LI) are 80 and 20% respectively (^1H and ^{31}P NMR data).

III. THE IMIDE-IMIDE REARRANGEMENT

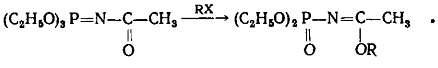
In the general case the imide–imide rearrangement can be represented schematically as follows:



where E = C or P, Y = O or S, and X–Z are electrophiles.

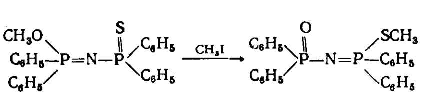
1. Rearrangement Under the Influence of Alkylating and Acylating Agents

The first example of the imide–imide rearrangement was observed by Kabachnik et al.[2] on heating triethyl acetylimidophosphate with alkyl halides (100–130°C, 4–6 h). This results in the formation of *O*-alkyl *N*-(diethoxyphosphoryl)iminoacetates, i.e. the rearrangement proceeds at the carbonyl oxygen atom:

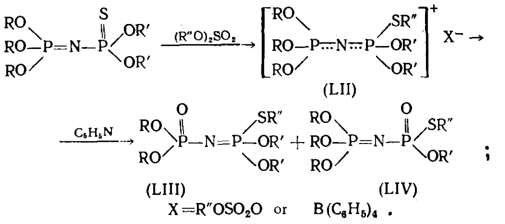


$$(C_2H_5O)_3P{=}N{-}\underset{\underset{O}{\|}}{C}{-}CH_3 \xrightarrow{RX} (C_2H_5O)_2\underset{\underset{O}{\|}}{P}{-}N{=}\underset{\underset{OR}{|}}{C}{-}CH_3 .$$

Thiophosphorylimidophosphates are alkylated usually at the thiono-sulphur atom. The reaction of *O*-methyl diphenyl(diphenylthiophosphorylimido)phosphinate with methyl iodide has been described[64]:



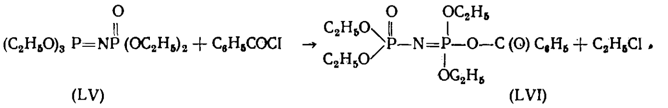
Khodak, Gilyarov, and Kabachnik[65,66] showed that the reaction of trialkyl dialkoxythiophosphorylimidophosphates with dialkyl sulphates proceeds via a stage involving the formation of quasi-phosphonium salts (LII), which decompose under the influence of nucleophiles with formation of the products of the imide-imide [compound (LIII)] and (or) thione-thiol [compound (LIV)] rearrangements:


(LII)

(LIII) (LIV)

X=R″OSO$_2$O or B(C$_6$H$_5$)$_4$.

The imide-imide rearrangement proceeds via the reaction of phosphorylimidophosphates with acylating agents. Thus in the reaction of triethyl diethoxyphosphorylimidophosphate (LV) with benzoyl chloride (10 h, 60°C) the acylation is directed to the phosphoryl oxygen atom and the anhydride (LVI) is formed, its structure being confirmed by ^{31}P NMR:


(LV) (LVI)

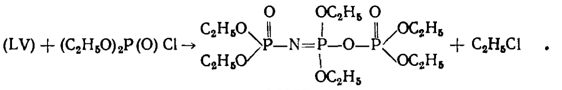
The presence of the anhydride linkage has been demonstrated by the reaction with cyclohexylamine from which cyclohexylbenzamide and the cyclohexylammonium salt of bis(diethoxyphosphoryl)imide (LVII) were isolated[18,67]:

$$\text{(LVI)} \xrightarrow{RNH_2} [(C_2H_5O)_2P(O)]_2NH \cdot RNH_2 + C_6H_5CONHR$$

(LVII)

R = cyclo-C$_6$H$_{11}$.

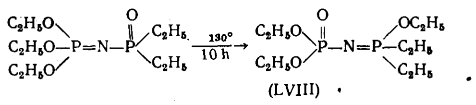
Diethyl phosphorochloridate reacts similarly to benzoyl chloride:


(LVIII)

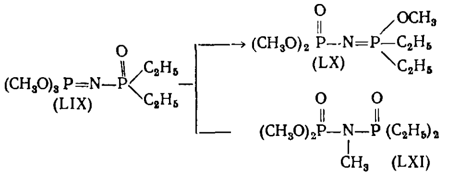
O-Ethyl N,N,N′,N′-tetraethyldiamido(diethoxyphosphorylimido)phosphate $C_2H_5O[(C_2H_5)_2N]_2P{=}NP(O)(OC_2H_5)_2$ reacts with benzoyl chloride and diethyl phosphorochloridate similarly to the imidophosphate (LV).[18,67]

2. Thermal Isomerisation

The imide-imide rearrangement of phosphorylimidophosphates was observed for the first time[3] in the thermal isomerisation of triethyl diethylphosphorylimidophosphate and has been called by the authors the "phosphazene-phosphoxide rearrangement":

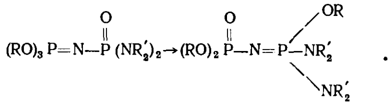

(LVIII) .

As shown in subsequent studies[53,68], the imide-imide rearrangement of phosphorylimidophosphates $(RO)_3P{=}NP(O)XY$ (X and Y are alkyl or phenyl groups) is of a general type. It proceeds readily for methoxy-derivatives. Thus even at 20°C trimethyl diethylphosphorylimidophosphate (LIX) undergoes partial isomerisation after a few days, and virtually complete isomerisation after four months, to the ester (LX); the product of the imide-amide rearrangement (LXI) is also formed as an admixture:


(LIX) (LX) (LXI)

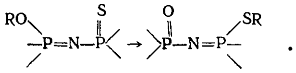
On thermal isomerisation, trialkyl alkoxyalkylphosphorylimidophosphates give rise to products of the imide-amide or imide-imide rearrangement, depending on the reaction conditions[54,69] (see Section II, subsection 3).

The imide-imide rearrangement with formation of the imidophosphates (LXII) is observed in the thermal isomerisation of trialkyl tetra-alkyldiamidophosphorylimidophosphates, the rate of isomerisation decreasing in the following sequence of groups R : $CH_3 > C_2H_5 > C_4H_9$:

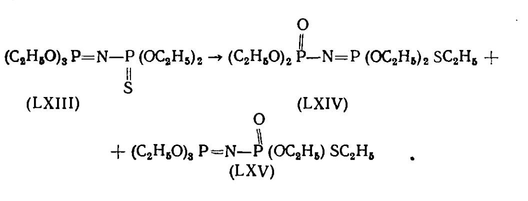

(LXII)

For example, trimethyl tetraethyldiamidophosphorylimidophosphate isomerises in 6 h at 85-90°C.[21]

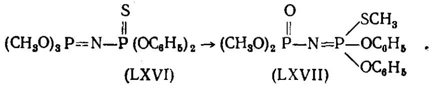
In the thermal isomerisation of thiophosphorylimidophosphates mainly the thiono-sulphur atom is attacked, i.e. the imide-imide rearrangement takes place:



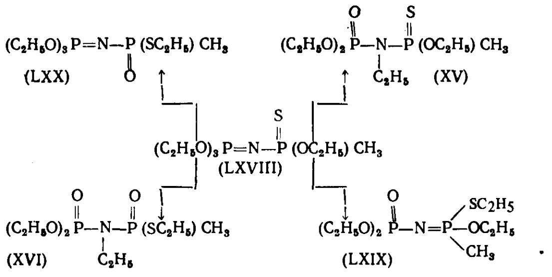
When triethyl diethoxythiophosphorylimidophosphate (LXIII) is heated (6 h, 140°C), the imidophosphates (LXIV) and (LXV) are formed[4,7]:


(LXIII) (LXIV) (LXV)

Attack on the sulphur atom occurs in the thermal isomerisation of trimethyl diphenoxythiophosphorylimidophosphate (LXVI) to the imidophosphate (LXVII)[70]:


(LXVI) (LXVII)

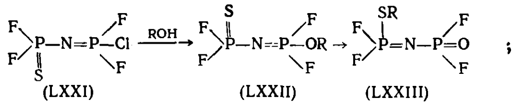
The thermal isomerisation of triethyl ethoxymethylthiophosphorylimidophosphate (LXVIII) (130°C, 10-11 h) takes place in a much more complex manner. A detailed study of this reaction[22] showed that, together with the main product O-ethyl S-ethyl (diethoxyphosphorylimido)methylphosphonate (LXIX) (77.4%), the isomers (XV), (LXX), and (XVI) are formed in small amounts (8.5, 10.4, and 3.7% respectively; GLC data):



(LXX) (XV) (LXVIII) (XVI) (LXIX)

According to earlier results[71], the thermal isomerisation of the imidophosphate (LXVIII) yields only (XV) under these conditions.

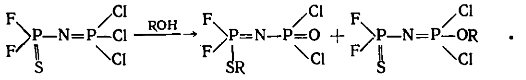
The introduction of a halogen atom at the phosphorus atom joined to the imide group in thiophosphorylimidophosphates increases sharply the rate of isomerisation. When difluorothiophosphorylimidophosphorus chloride difluoride (LXXI) reacts with methanol or ethanol[72,73], the resulting esters (LXXII) isomerise to the thioesters (LXXIII) already during the reaction:



(LXXI) (LXXII) (LXXIII)

R = CH3, or C2H5.

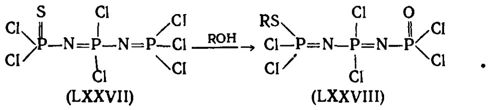
Such isomerisation is difficult for the products of the reaction of difluorothiophosphorylimidophosphorus trichloride (LXXIV) with alcohols:



(LXXIV) (LXXV) (LXXVI)

Thus the decrease of the electronegativity of the substituents at the phosphorus atom joined to the imide group (on passing from fluorine to chlorine) hinders the isomerisation.

The *S*-isomers (LXXVIII) were isolated in the reaction between (LXXVII) and methanol or ethanol (at 20°C) [75]:



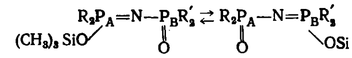
(LXXVII) (LXXVIII)

Consequently the removal of the alkylating group RO to the $(-N{=}PCl_2-)$ fragment does not affect the ease of isomerisation.

3. Rearrangement with Participation of the Trimethylsilyl Group

In all the instances considered hitherto the imide-imide rearrangement was irreversible.

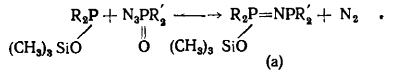
It has been found[62,76] by $^{31}P-\{^1H\}$ NMR that the trimethylsilyl group in many phosphorylimidophosphates [(LXXIX)-(LXXXIV)] undergoes both reversible [(a)⇌(b)] and irreversible [(a)→(b)] transfers:



(LXXIX): $R{=}R'{=}OCH_3$; (LXXX): $R{=}R'{=}OC_2H_5$;
(LXXXI): $R{=}OC_2H_5$, $R'{=}OC_4H_9$-iso; (LXXXII): $R'{=}OC_2H_5$, $R'{=}N(CH_3)_2$; (LXXXIII): $R{=}OC_2H_5$, $R'{=}C_2H_5$;
(LXXXIV): $R{=}OCH_3$, $R'{=}OC_2H_5$.

A reversible transfer of the trimethylsilyl group has been observed for the imidophosphates (LXXIX)-(LXXXI) (the spectrum contains one broad signal at room temperature and an AB-quartet due to the two non-equivalent phosphorus atoms appears at a reduced temperature where exchange is inhibited). The observed changes in the spectrum as a function of temperature indicate the occurrence of slow (in terms of the NMR time scale) exchange. This made it possible to determine the lifetime τ of each isomeric form.

An irreversible transfer of the trimethylsilyl group has been observed for the imidophosphates (LXXXII)-(LXXXIV). On the basis of the scheme used for the synthesis, compounds (a) should have been formed in the absence of a rearrangement:



However, in fact the compounds obtained have a structure corresponding to form (b) according to $^{31}P-\{^1H\}$ NMR spectra, i.e. under the reaction conditions the trimethylsilyl group passes to the phosphoryl oxygen linked to the P_B atom.

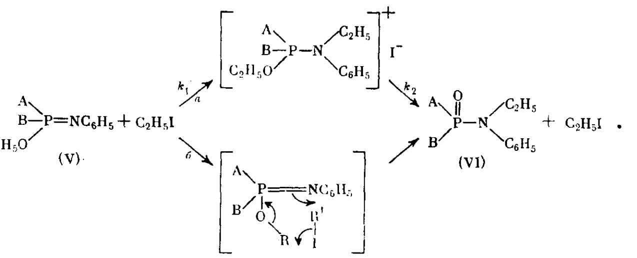
Later Riesel and coworkers[77,78] reported the reversible migration of the trimethylsilyl group in the "symmetrical" imidophosphates $[(CH_3)_3SiO]R_2P{=}NP(O)PR_2$ (R is an alkoxy or a dialkylamido-group) on the basis of ^{31}P NMR spectra.

The reversible migration of other groups (ethyl, benzoyl, or benzyl) in the imidophosphates $R_2(XO)P{=}NP.(O)R_2$ [$R = OC_2H_5$, $X = C_2H_5$ or C_6H_5CO; $R = N(C_2H_5)_2$, $X = C_6H_5CH_2$] could not be observed at temperatures between −80°C and +90°C according to $^{31}P-\{^1H\}$ NMR data[76].

IV. THE MECHANISMS OF THE IMIDE-AMIDE AND IMIDE-IMIDE REARRANGEMENTS

There have been few studies devoted to the investigation of the mechanisms of the above rearrangements. In some cases only hypotheses concerning the mechanism have been put forward.

As stated above, the kinetics of the reaction of ethoxy(phenylimido)phosphorus compounds (V) with ethyl iodide have been studied[11,13,14]. Two alternative pathways had been suggested previously to account for the mechanism of the imide-amide rearrangement[1]: (a) a two-stage pathway with an intermediate quasi-phosphonium compound (b) a single-stage pathway with a cyclic transition stage:

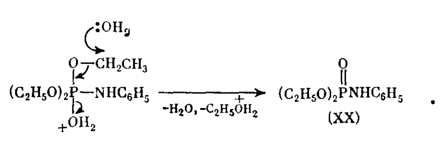


The logarithms of the rate constants listed in the Table are linearly correlated with σ^{ph} for the substituents at the phosphorus atom:

$$\lg k = 3.44 - 0.604 \sum \sigma^{ph} \ .$$

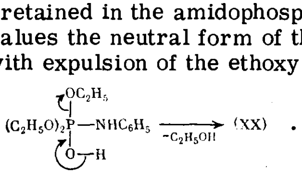
The low absolute value of the correlation parameter $\rho = 0.604$ supports a cyclic transition state, i.e. mechanism (b).

The study of the mechanism of the hydrolysis of triethyl phenylimidophosphate (I) in the presence of $H_2{}^{18}O$ at different pH (between 2 and 8) showed[79] that the content of ^{18}O in the hydrolysis products depends on pH [from 22% at low pH values (pH ~ 2) to 80% at high pH values (pH ~ 8)]. The authors[79] suggest that at low pH values the adduct of the protonated imidophosphate and water is dealkylated under the influence of another water molecule with elimination of the water molecule which had added on initially:



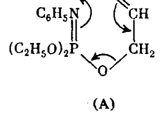
Under these conditions, all the oxygen atoms in the imidophosphate (I) are retained in the amidophosphate (XX).

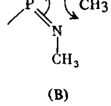
At higher pH values the neutral form of the intermediate may decompose with expulsion of the ethoxy-group:



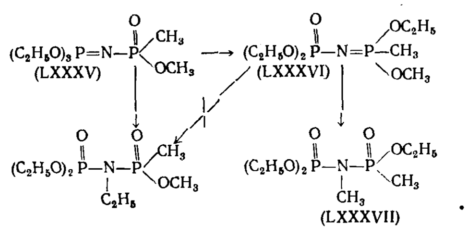
It is suggested that this entails an increase of the content of labelled oxygen in the amide (XX) formed.

The mechanism of the thermal isomerisation of aryl or alkyl imidophosphates has not been specially studied. Pudovik and coworkers[33,34] investigated the thermal isomerisation of *O*-allyl phenylimidophosphates and concluded that it is an intramolecular process with a cyclic transition state (A) (the reaction is accompanied by the inversion of the allyl group). Referring to these results, Goldwhite et al.[40] suggested that the thermal isomerisation of trimethyl methylimidophosphate also proceeds via the intramolecular mechanism (B):


(A)

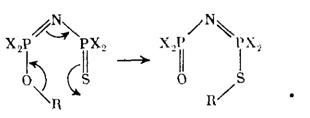

(B)

A study of the isomerisation of triethyl methoxymethylphosphorylimidophosphate (LXXXV) by ^1H NMR showed[69] that an imide–imide rearrangement takes place initially with formation of the imidophosphate (LXXXVI) and then, after further heating, it is followed by an imide–amide rearrangement; the methyl group then migrates to the nitrogen atom and compound (LXXXVII) is formed:

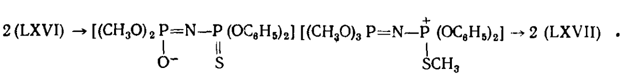


As regards the mechanism of the imide–imide rearrangement of phosphorylimidophosphates, it has been suggested that the reaction is intermolecular in the case of trialkyl dialkylphosphorylimidophosphates[68] or triethyl methoxymethylphosphorylimidophosphate (LXXXV).[69]

It has been suggested[74] that the conversion of *O*-alkyl dihalogeno(dihalogenothiophosphorylimido)phosphates into the *S*-alkyl isomers is likewise an intramolecular process and can be represented schematically as follows:

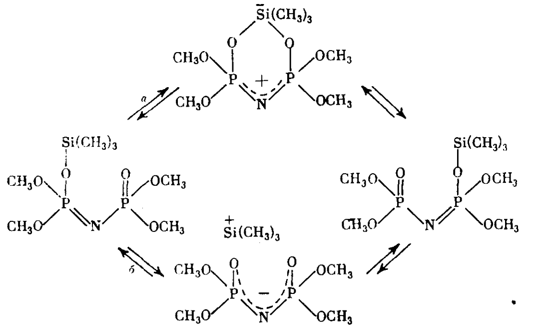


Khodak et al.[70] studied the mechanism of the imide–imide rearrangement in relation to the thermal isomerisation of trimethyl diphenoxythiophosphorylimidophosphate (LXVI). The kinetics of the isomerisation at 98°C in bromobenzene are described satisfactorily by a second-order equation [$k = (6.3 \pm 0.3) \times 10^{-5}$ litre mole^{-1} s^{-1}]. Having investigated the influence of temperature and the dielectric constant of the medium on the isomerisation rate constant, the authors[70] concluded that the mechanism involving intermolecular alkylation with a low-polarity transition state and the formation of an ion pair as a rapidly reacting intermediate is most probable for the isomerisation of the imidophosphate (LXVI) to the imidophosphate (LXVII):



$$2\,(\mathrm{LXVI}) \rightarrow [(CH_3O)_2\underset{O^-}{P}{=}N{-}\underset{S}{\overset{}{P}}(OC_6H_5)_2]\,[(CH_3O)_3P{=}N{-}\underset{SCH_3}{\overset{+}{P}}(OC_6H_5)_2] \rightarrow 2\,(\mathrm{LXVII}) \ .$$

In order to elucidate the mechanism of the migration of the trimethylsilyl group (see above), the order of the reaction of dimethyl trimethylsilyl dimethoxyphosphorylimidophosphate (LXXIX) was determined. The dependence of the lifetime of one of the tautomeric forms [the lifetimes are the same for the imidophosphate (LXXIX)] on concentration was investigated by ^1H NMR.[76] It was found that at the same temperature the lifetimes are the same in solutions at different concentrations (in chloroform). This shows that the reaction is of first order, i.e. that the imidophosphate (LXXIX) undergoes an intramolecular rearrangement. Mechanism *a* involving the formation of a cyclic intermediate, may be proposed for the rearrangement, in view of the presence of the unshared *d* orbitals of the silicon atom. Nor can one rule out the ionic mechanism *b*—the migration of the trimethylsilyl group as a cation:



Examination of the data for the imide–amide and imide–imide rearrangement permits the conclusion that the IPC containing the $R{-}O{-}\underset{|}{\overset{|}{P}}{=}N{-}$, $R{-}O{-}\underset{|}{\overset{|}{P}}{=}N{-}\overset{|}{P}{=}O$, and $R{-}O{-}\underset{|}{\overset{|}{P}}{=}N{-}\underset{|}{\overset{|}{P}}{=}S$ groups are highly reactive.

In many instances these rearrangements may be used as a method for the synthesis of new IPC and phosphorus acid amides.

The results of the study of the thermal isomerisation permit the conclusion that, owing to the high lability of the IPC, their synthesis in a pure form requires special checks (by thin-layer chromatography, infrared spectroscopy, ^{31}P NMR, and ^{1}H NMR).

Since certain types of IPC may have practical applications as drugs[90], herbicides[81,82], and defoliants[83], the importance of studies on the imide–amide and imide–imide rearrangements can be readily understood. This field of the IPC chemistry is developing vigorously; we may expect that it will yield new interesting theoretical and practical results.

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Organic Phosphorus Compounds with a P-P Bond

I.F.Lutsenko and M.V.Proskurnina

Data on the methods of synthesis and reactivities of organic diphosphines with a direct P-P bond between four-coordinated phosphorus atoms as well as compounds with a P-P bond between a three-coordinated phosphorus atom and a phosphorus atom with a higher degree of coordination are surveyed and described systematically. Problems of the steric structures and the results of structural analysis, spectroscopic studies, and studies by other methods are considered.
The bibliography includes 269 references.

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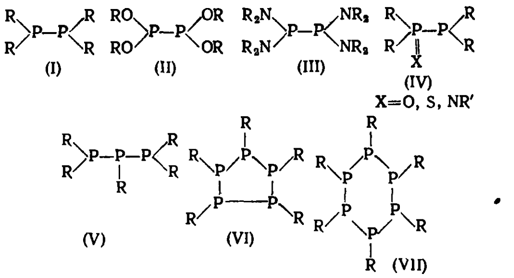
I. INTRODUCTION

Studies on organic compounds with P–P bonds have continued since 1877 when Kohler and Michaelis[1] obtained for the first time the so-called phosphobenzene[1]:

$$n\,\mathrm{PhPCl_2} + n\,\mathrm{PhPH_2} \rightarrow 2\,(\mathrm{PhP})_n + 2n\,\mathrm{HCl}.$$

Numerous classes of organophosphorus compounds (OPC) with P–P bonds are now known; these compounds can be fairly formally classified as follows: (a) in terms of the valence state of the phosphorus atoms linked to one another; (b) in terms of the number of phosphorus atoms in the chain; (c) in terms of the number of phosphorus atoms in the ring. For example, it is possible to distinguish the following types of organic compounds with P–P bonds: tetra-alkyl(aryl)-diphosphines† (I), tetra-alkoxy(aryloxy)-diphosphines (II), tetra-aminodiphosphines (III), tetra-alkyl-(aryl)diphosphine monoxides (monosulphides, monoimides), tetra-alkyl(aryl)diphosphines (IV), penta-alkyl(aryl)triphosphines (V), polyalkyl(aryl)cyclopolyphosphines (VI) and (VII), etc.



A review published in 1965 is devoted to organic diphosphines[2]. Since then the number of data on this subject has significantly increased and in the present review we shall therefore consider only compounds with a P–P bond between two phosphorus atoms at least one of which is three-coordinated; mainly studies published after the above review[3] or not included in it are analysed.

II. THE STRUCTURES OF ORGANIC DI- AND POLY-PHOSPHINES

The length of the P–P bond in organic di- and polyphosphines is ~ 2.22 Å,[4] is fairly constant, and does not deviate significantly from the value (2.24 Å) predicted by Pauling[5], which suggests either the absence of a higher degree of binding than in a simple σ bond or the presence of a constant additional binding. The latter is unlikely, since the length of the P–P bond is almost independent of the substituent, its electronegativity, or whether the molecular structure is cyclic or non-cyclic and even of the valence state of the phosphorus atom (Table 1). Thus the lengths of the P–P bond in tetramethyldiphosphine, diphosphine, and tetrakis(trifluoromethyl)diphosphine are 2.192, 2.216, and 2.160 Å respectively, while in the presence of the most electronegative substituent (fluorine) the longest P–P bond is formed (2.281 Å) (Table 1). The length of the P–P bond in diphosphine is not a simple function of the electronegativity of the groups and no evidence for the existence of $p\pi - d\pi$ conjugation can be obtained from the lengths of these bonds. However, even in difluorodiphosphine, where the greatest delocalisation should be expected, neither the bond length nor the conformation of the molecules (see below) permit the conclusion that $p\pi - d\pi$ conjugation obtains[7]. The Nyholm–Gillespie theory and semiempirical calculations predict satisfactorily the bond lengths and angles in organic phosphines[8-10] but have no predictive power as regards organic diphosphines[12,13]. On the other hand, *ab initio* calculations yield P–P bond lengths in good agreement with experiment[12,13].

Table 1. The P–P bond lengths.

Compound	P–P bond length, Å	Refs.	Compound	P–P bond length, Å	Refs.
$H_2P—PH_2$	2.218±0,004	6	$Me_2P—PMe_2 \cdot 2Fe(CO)_4$	2,231±0.007	19
$D_2P—PDH$	2.219±0,0004	15	$Ph_2P—PPh_2 \cdot 2Ni(CO)_3$	2,277±0,004	20
$D_2P—PF_2$	2.218±0,038	6	$Et_2P(S)—P(S)Et_2$	2.220±0,01	21
$I_2P—PI_2$	2.21±0.06	16	$(PhP)_5$	2,217±0,006	22,23
$F_2P—PF_2$	2.281±0.03	14,11	$(PhP)_6$	2,233±0,005	24,25
$Me_2P—PMe_2$	2,192±0.18	17	$(PCF_3)_4$	2,213±0,005	26
$(F_3C)_2P—P(CF_3)_2$	2,182±0.016	6	$(PCF_3)_5$	2,223±0,007	27
$Me_2P—PMe_2 \cdot 2BH_3$	2,204±0.005	18			

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† The term "diphosphanes" has also been suggested for organic diphosphines on the basis of the analogy between these compounds and organic disilanes, distannanes, etc.[2]: however, it does not reflect the valence state of the phosphorus atoms.

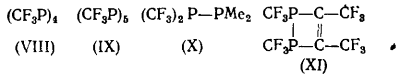
The C–H and C–P bond lengths and the C–P–C and C–H–P dihedral angles in Me_4P_2 are close to the value in Me_nPH_{4-n} (n = 1–3).[3]

The P–P bond dissociation energies in diphosphine, measured mass-spectrometrically, are 61[28] and 74[29] kcal mole^{-1} for P_2H_4, 62 kcal mole^{-1} [30] for P_2Cl_4, 71 kcal mole^{-1} [28] for P_2I_4, and 86 kcal mole^{-1} [32] for Et_4P_2, but these data are subject to large systematic errors[28]. According to data obtained by other methods, the P–P bond energy varies from 44 to 58 kcal mole^{-1} (Table 2), which is significantly less than the energies of the P–N (67–77 kcal mole^{-1}) and P–C (65–71 kcal mole^{-1}) bonds[5,38,39], but is higher than the energy of the N–N bond (in N_2F_4, for example, the latter is 20.4 ± 1.3 kcal mole^{-1} [32]).

Table 2. The P–P bond energies.

Compound	P–P bond energy, kcal mole^{-1}	Method of determination	Refs.
$H_2P—PH_2$	46.8	Thermochemical	34
P_4	51,3	Calculation	35
P_4	51,3	Thermochemical	5
P_4	44	Spectroscopic	36
$Ph_2P—PPh_2$	50	Thermochemical	37

Experimental evidence for a planar configuration of the phosphorus atoms, which might indicate the occurrence of $p\pi - d\pi$ binding, has not been obtained for phosphines having the general formula $R_2P–PR_2$ either in the gas or in the solid phase. *Ab initio* calculations by the SCF LCAO-MO method for all the possible rotational isomers of the P_2H_4 molecule also indicate the absence of $p\pi - d\pi$ binding[40]. According to photoelectron spectroscopic data for di- and poly-phosphines (VIII)–(XI), the degree of $p\pi - d\pi$ binding is very insignificant[41]:

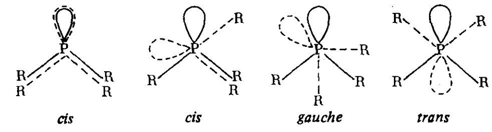


$(CF_3P)_4$ (VIII) $(CF_3P)_5$ (IX) $(CF_3)_2P—PMe_2$ (X)

$$\begin{matrix} CF_3P—C—CF_3 \\ | \quad\;\; \| \\ CF_3P—C—CF_3 \end{matrix}$$

(XI)

The substituents and the lone electron pair of the X atom in molecules having the general formula X_2Y_4*, where X = N, P, or As, have a pyramidal arrangement; in this case there is a possibility of three types of symmetry—C_2 (*cis*- and *gauche*), C_{2v} (*cis*), and C_{2h} (*trans*).[42]



Symmetry	C_{2v}	C_2	C_2	C_{2h}
Dihedral angle	0°	46°55′	93°50′	180°

The relative number of conformations, determined by their stabilities, depends in the general case on the interaction of the two lone electron pairs, on the steric repulsion between the substituents, on the electrostatic interaction, and other factors. Table 3 presents data for the conformational compositions of a series of inorganic and organic diphosphines. Evidently the *gauche*- or *trans*-conformation is the most stable. The proportion of the *trans*-conformer can be related in certain cases to the electronegativity of the substituents at the phosphorus atom: thus the contents of the *trans*-conformers of Me_4P_2 and Cl_4P_2 are respectively 40 and 95%[42–45]. This effect may be attributed wholly to the difference between the electronegativities of the Me group and the Cl atom (2.0 and 3.0 respectively), since the effective volumes of the substituents and the P–P bond lengths in these compounds are identical. This conclusion has also been confirmed by a comparison of the conformational compositions of $(CF_3)_4P_2$ and F_4P_2 (the electronegativities of the CF_3 group and the fluorine atom are 3.2 and 4 respectively); the content of the *gauche*-form of $(CF_3)_4P_2$ is much higher[46]. In this case steric hindrance is also apparently unimportant, since the P–P bond in $(CF_3)_4P_2$ is much shorter (2.16 Å) than in F_4P_2 (2.28 Å). If $(CF_3)_4P_2$ and Me_4P_2 are compared from this point of view, the latter should have the *gauche*-conformation and the former should exist as the *trans*-conformer. However, the shorter P–P bond in the perfluoro-compound prevents this and the contents of the *gauche*-conformers of $(CF_3)_4P_2$ and Me_4P_2 are 30 and 60% respectively.

Table 3. The P–P bond lengths in inorganic and organic diphosphines.

Compound	Conformational composition	Method of determination	Refs.
$H_2P—PH_2$	*gauche* (in solution)	RS*	6,15,47
$H_2P—PH_2$	*trans* (in solution)	RS	48
$H_2P—PH_2$	*gauche* (gas)	RS	49
$H_2P—PH_2$	*trans* (solid)	i.r. and RS	50
$H_2P—PH_2$	*gauche* > *cis* > *trans*	SCF and EHM** methods	10
$H_2P—PH_2$	*gauche* (10% *trans*)	PES***	51
$H_2P—PH_2$	*gauche* > *trans* > *cis*	*ab initio* calculation	52
$H_2P—PH_2$	*gauche*	*ab initio* calculation	13,40
$Me_2P—PMe_2$	*gauche* (60%) *trans* 40%) (liquid, gas)	i.r. and RS	43,44
$Me_2P—PMe_2$	*trans, gauche*	PES	54
$Me_2P—PMe_2$	*gauche*	PES	53
$Et_2P—PEt_2$	*trans* (solid)	i.r. and RS	43
$Et_2P—PEt_2$	*trans*	^1H NMR	55
Me(Et)P—P(Et)Me	*gauche* (liquid)	^{13}C NMR; ^1H NMR	56
Me(iso-Pr)P-P(iso-Pr)Me	*gauche* (liquid)	^{13}C NMR; ^1H NMR	56
Me(t-Bu)P-P-(t-Bu)Me	*gauche* (liquid)	^1H NMR; ^{31}P NMR	57
$Me_2P-P(t-Bu)_2$	*gauche* (liquid)	^{13}C NMR; ^1H NMR	56
$(iso-Pr)_2P-P(Pr-iso)_2$	*gauche* (liquid)	^{13}C NMR; ^1H NMR	56
$(t-Bu)_2P-P(But)_2$	*gauche* (5% *trans*) (liquid)	^{13}C NMR; ^1H NMR	58,59
$Cl_2P—PCl_2$	*trans* (95%) (liquid, solid)	i.r. and RS	45
$Cl_2P—PCl_2$	*trans* (95%)	CNDO and *ab initio* calculation	15
$Cl_2P—PCl_2$	*trans* (liquid)	Calculation by Kreevoy and Mason's method (Ref.60)	61
	trans (<10% *gauche*) (gas)	gas electron diffraction	62
	trans > *gauche* > *cis*	*ab initio* calculation	13
	gauche > *cis* > *trans*	SCF method	10
	trans (liquid)	i.r. and RS	63,64
	trans (90%), *gauche* (10%)	PES	65
	trans (in solution, solid)	RS	16,66
	gauche (in solution)	i.r.	67,68
	trans (in solution)	Calculation by Kreevoy and Mason's method(Ref.60)	61

*Raman spectroscopy (Ed. of Translation).

**Extended Hückel method (Ed. of Translation).

***Photoelectron spectroscopy.

Nevertheless, mainly the *gauche*-conformation obtains for the majority of organic diphosphines, which confirms the rule of the greatest stability of the conformer with the *gauche*-disposition of the lone pairs (the *gauche*-effect)[69,70]. In the solid phase the diphosphines investigated exist in the *trans*-conformation, which may be a consequence of their packing in the crystal[69].

The conformational behaviour of diphosphines differs somewhat from that of their nitrogen analogues—hydrazine and its derivatives: the *gauche*-conformation obtains exclusively for hydrazine and tetramethylhydrazine in the gas, liquid, and solid states[71-75] and a 50% content of the *trans*-conformer has been found only for tetrafluorohydrazine in the gas and liquid states[76-78].

Photoelectron spectroscopy (PES) has been resorted to recently in order to determine the conformational compositions of organic diphosphines. On the basis of PES data, the diphosphines Me_4P_2 and $(CF_3)_4P_2$ are regarded as mixtures of *gauche*- and *trans*-conformers[54]; however, Ames and Turner[53] treat PES data for Me_4P_2 as confirmation of the existence of the latter exclusively as the *gauche*-conformer.

The barriers to rotation about the P–P bond (calculated data) are presented in Table 4; there are no experimental literature data. According to calculations by the *ab initio* SCF LCAO-MO method, the barrier to rotation in diphosphine is 3.3 kcal mole^{-1},[79] while in hydrazine the corresponding value is 11.5 kcal mole^{-1} according to the same method of calculation and experimental data. This difference between the barriers is logically consistent with the greater P–P bond length compared with $\ddot{N}$–$\ddot{N}$ and also with the greater diffuseness of the orbitals of the phosphorus atoms compared with those of the nitrogen atom[80].

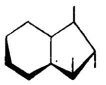
Table 4. The barriers to rotation about the P–P bond (kcal mole^{-1}).[13,15,63,64].

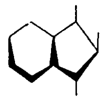
Compound	Method of calculation			
	EHM	SCF LCAO-MO	CNDO/2	*ab initio*
$H_2P—PH_2$	1.8 (*cis*)	9.2 (*cis*)	1.3 (*cis*)	4.1 (*cis*) ; 0.6 (*trans*)
$H_2P—PH_2$	4.9 (*trans*)	—	6.9 (*trans*)	2.3 (*cis*) ; 0,5 (*trans*)
$F_2P—PF_2$	4.6 (*cis*)	0.3 (*cis*); 3.9 (*trans*-)	24.8 (*cis*)	4.9 (*trans*)
$F_2P—PF_2$	6.7 (*trans*)	4.9 (*cis*); 4.3 (*trans*)	31.6 (*trans*)	
$H_2P—PF_2$	—	12.0 (cis)	—	—
$H_2P—PF_2$	—	6.8 (*trans*)	—	—

If there are two different substituents at the same phosphorus atom in the organic diphosphine $R^1(R^2)P-P(R^1)(R^2)$, then the topology of this system is analogous to that of the system with two asymmetric carbon atoms: the lone electron pair plays the role of the fourth substituent. Indeed asymmetric organic diphosphines have the *meso*- and *d*, *l*-forms, whose interconversion (22–24 kcal mole^{-1}) involves rotation about the P–P bond and inversion of the phosphorus pyramid[81,82]. The main contribution to the transition energy comes from the energy of the inversion process, which is lower in diphosphines than in trialkylphosphines. Bulky and electron-donating substituents lower the inversion barrier, the influence of electronic factors predominating as a rule. The proportions of the racemate and the *meso*-form in solution are approximately the same for sterically non-hindered substituents (R^1 = Me, R^2 = Et). When R^1 = Me and R^2 = t-Bu, the *meso*-form is absent and (XII) exists as the racemate. Indeed in the two possible rotational *gauche*-isomers the bulky R^2 groups in the *meso*-form are brought closer together and their *gauche*-steric interaction is unfavourable. According to ^1H and ^{31}P NMR data, at 130–150°C equilibrium is attained rapidly (in terms of the NMR time scale) between the two diastereoisomers[83-85].

A large number of structures have been proposed for cyclic polyphosphines. Thus all structures, ranging from dimeric to polymeric, have been discussed for phosphobenzene. It has now been established that in the crystalline state phosphobenzene exists as the pentamer or hexamer (or their mixture)[22,25,86-88]. As a rule, standard methods of synthesis lead to a mixture with the preferential formation of the pentamer, but, if the reaction between dichlorophenylphosphine and phenylphosphine is carried out in tetrahydrofuran (THF), mainly the hexamer is obtained. On crystallisation from acetonitrile, it is possible to isolate the pure pentamer, whose molecule has the structure of a flat ring where the phenyl groups are located in the plane of the ring and the deviations from the $D_{5}d$ symmetry are extremely insignificant[22]. The hexamer is polymorphic and exists in four modifications—monoclinic, orthorhombic, triclinic, and trigonal. The triclinic modification has the chair conformation with the equatorial disposition of the benzene rings[24,88]. The behaviour of phosphobenzene in solution is unusual: according to molecular weight determinations, both the pentamer and hexamer decompose to the tetramer and even the trimer; on the other hand, crystallisation from solution again leads solely to the pentamer and hexamer. In order to explain this, it is assumed that the P–P bonds readily dissociate in solution[23,89]—possibly with the intermediate formation of the phosphorus analogue of carbene, namely RP:[89]. In the solid phase rapid interconversion does not occur: thus, after two and a half years, the phosphobenzene hexamer was converted into the pentamer to the extent of only 50%.[90] Despite the large radius of the phosphorus atom, the size of the ring depends greatly on the nature of the substituent. Thus ethyl- and butyl-phosphorus consist as a rule of equal amounts of the tetramer and pentamer, but do not form hexamers[91-93]; propyl- and cyclohexyl-phosphorus are tetrameric in solution and in the solid state with the *trans*-position of the lone electron pairs[94,95]. Only the pentameric form [pentakis(pentafluorophenyl)pentaphospholane] has been found for pentafluorophenylphosphine[96].

Structural analysis of carbocyclic compounds with P–P bonds has undoubtedly revealed interesting characteristics of these substances. Hitherto the number of known compounds of this kind is comparatively small. Thus the configuration of the *trans*, *trans*-isomer has been established for 1,2,3-triphenyl-1,2,3-triphosphaindan in the crystalline state[25]:


trans, trans


cis, trans

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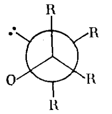
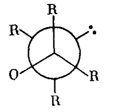
According to NMR data[25], phosphaindan exists as the *cis*, *trans*-isomer in solution, in good agreement with its reactivity as a ligand in the reaction with iron carbonyls[97]. 1,2,3,4-Tetraphenyl-1,2,3,4-tetraphospholane[98] exists in the stable half-chair conformation, where all the phenyl groups are axial (C_2 symmetry).

The existence of two rotational isomers, (XII) and (XIII), may be expected for organic diphosphine monoxides, but these cannot be identified on the basis of ^{31}P NMR data (the spectra of tetra-alkyldiphosphine monoxides do not change between −90° and +30° C)[99]:



(XII)



(XIII)

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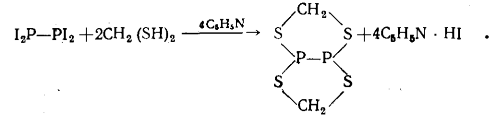
III. METHODS OF SYNTHESIS

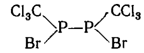
At least two fundamentally different approaches to the synthesis of OPC with P–P bonds are possible: the first consists in the use of starting compounds already containing a P–P bond and in the second the P–P bond is formed during synthesis. In the first case it would appear convenient to employ the readily available tetra-iododiphosphine[100], but numerous attempts to use it (in reactions with alcohols, amines, alkyl halides, and organometallic compounds) have led as a rule to products with a single phosphorus atom in the molecule[101–104]. As an exception, one may mention the following reactions, which take place with extremely low yields[100,101]:

$$I_2P{-}PI_2 + 4AgCN \rightarrow (CN)_2P{-}P(CN)_2 + 4AgI \;,$$

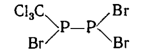


In a study of the alkylation of phosphorus di-iodide Kirsanov and coworkers[105–109] developed a convenient method for the synthesis of symmetrical diaryldi-iododiphosphines.

Phosphorus dichloride $(PCl_2)_2$ has been hardly used in syntheses, since it is difficult to obtain[110]. There have been few examples of the use of elemental phosphorus, which already contains P–P bonds. Thus ultraviolet irradiation of a solution of elemental phosphorus in bromotrichloromethane gives satisfactory yields of (XIV) and (XV)[110]:



(XIV)



(XV)

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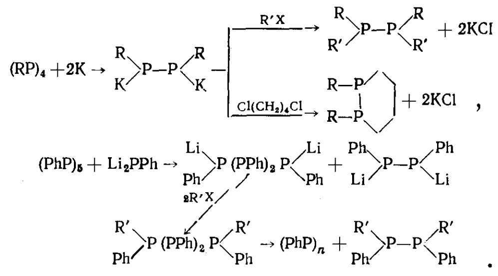
The reactions, which take place in the gas phase, are undoubtedly unsuitable for preparative purposes, but the following interesting reaction may be mentioned[111]:

$$P_4 + 4CHF_3 \rightarrow (F_3CP)_4 + 2H_2 \;.$$

The use of elemental phosphorus made it possible to obtain a very unusual molecule with a P–P bond between two two-coordinated phosphorus atoms (in the complex)[112]:

$$P_4 + 2(C_5H_5)_2Mo \cdot H_2 \xrightarrow[95^\circ]{\text{toluene}} 2(C_5H_5)_2Mo \cdot HP{=}PH \;.$$

Red phosphorus reacts smoothly with sodium in liquid ammonia to form diphosphides, which can then be alkylated by alkyl halides to form tetra-alkyldiphosphines[113,114]. The necessity to carry out experiments in liquid ammonia and the comparatively low yields (not exceeding 25%), due to the cleavage of Alk_4P_2 to sodium phosphide, limit the applicability of this reaction. On the other hand, the ability of the P–P bonds to dissociate under the influence of alkali metals and a number of other nucleophiles has been used to synthesise di- and poly-phosphines from cyclopolyphosphines, which are frequently more readily available than other compounds with P–P bonds[115–121]:



This method makes it possible to obtain a wide range of symmetrical and asymmetric organic diphosphines, as well as new compounds with a P–P bond in the ring, in 70–90% yields.

A very convenient preparative method for the synthesis of organic compounds with P–P bonds from inorganic phosphorus compounds was proposed by Kabachnik and coworkers and was subsequently developed by other investigators[122–125]:

$$RMgX + P(S)Cl_3 \rightarrow R_2P(S){-}P(S)R_2 + MgXCl \;,$$
$$R_2P(S){-}P(S)R_2 \xrightarrow{2R_3P} R_2P{-}PR_2 + 2R_3P{=}S \;.$$

Tetra-alkyldiphosphine disulphides are formed in yields greater than 60% and are reduced by metals as well as trialkylphosphines and trialkyl phosphites to tetra-alkyldiphosphines[81,82,126].

Numerous examples of the synthesis of organic diphosphines from halogenophosphines on treatment with various metals or metal phosphides via the general mechanism

$$R_2PX + M \rightarrow R_2PM \xrightarrow[-MX]{R_2PX} R_2P{-}PR_2 + MX$$

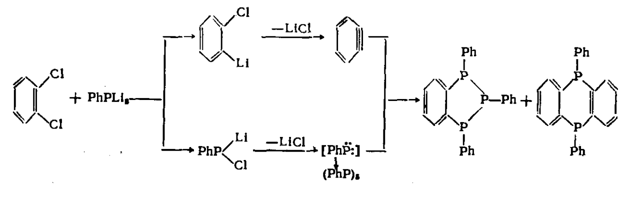
have been described in Cowley's review[3]; here we shall confine ourselves to new examples of this widely used method[63,127–129,131–135]:

$$2(C_6F_5)_2PBr + Hg \rightarrow (C_6F_5)_2P{-}P(C_6F_5)_2 + Hg_2Br_2 \;,$$
$$2F_2PI + 2Hg \rightarrow F_2P{-}PF_2 + Hg_2I_2 \;,$$
$$Ph_2PNa + ClP(NMe_2)_2 \rightarrow Ph_2P{-}P(NMe_2)_2 + NaCl \;,$$
$$(F_3C)_2P{-}SiMe_3 + IPH_2 \rightarrow (F_3C)_2P{-}PH_2 + Me_3SiI \;,$$
$$2RMgX + PCl_3 \xrightarrow[2MgXCl]{} [R_2PCl] \xrightarrow{Mg} R_2P{-}PR_2 + MgCl_2 \;,$$
$$2\,(t\text{-}Bu)_2PCl + Na \rightarrow (t\text{-}Bu)_2P{-}P(Bu\text{-}t)_2 + NaCl.$$

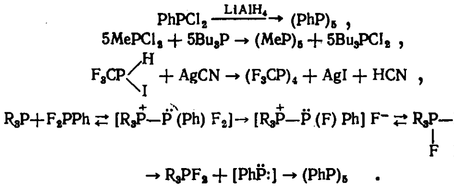
The condensation principle proved to be convenient also for the synthesis of cyclopolyphosphines using alkyldichlorophosphines in the reaction[91,134]:

$$4t\text{-}BuPCl_2 + 8Na \rightarrow (t\text{-}BuP)_4 + 8NaCl \;,$$
$$F_3CPI_2 + Hg \rightarrow (F_3CP)_4 + (F_3CP)_5 + HgI_2 \;.$$

Presumably in these and analogous instances the reaction proceeds via the phosphinidene $R\ddot{P}$:—the phosphorus analogue of carbene, which has two lone electron pairs and vacant 3*d* and 4*d* orbitals in the singlet configuration. The formation of phosphinidene is possible also in the following case[117]:



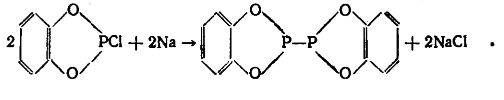
The generation of phosphinidene can apparently also be postulated in reactions of the following kind[134-137]:



$$PhPCl_2 \xrightarrow{LiAlH_4} (PhP)_5\ ,$$
$$5MePCl_2 + 5Bu_3P \rightarrow (MeP)_5 + 5Bu_3PCl_2\ ,$$
$$F_3CP(H)(I) + AgCN \rightarrow (F_3CP)_4 + AgI + HCN\ ,$$
$$R_3P + F_2PPh \rightleftarrows [R_3\overset{+}{P}-\overset{+}{P}(Ph)F_2] \rightarrow [R_3\overset{+}{P}-\ddot{P}(F)Ph]F^- \rightleftarrows R_3P(F)-\ddot{P}(F)Ph \rightarrow$$
$$\rightarrow R_3PF_2 + [Ph\ddot{P}:] \rightarrow (PhP)_5\ .$$

The esters and amides of hypodiphosphorous acid have been obtained from phosphorochloridites using sodium and potassium as well as mercury derivatives[138-141]:

$$(Me_3Si)_2Hg + 2(RO)_2PCl \rightarrow (RO)_2P-P(OR)_2 + 2Me_3SiCl + Hg\ ,$$
$$(Me_3Si)_2Hg + 2(Et_2N)_2PCl \rightarrow (Et_2N)_2P-P(NEt_2)_2 + 2Me_3SiCl + Hg\ ,$$



As will be shown below, the reactivity of organic diphosphines depends significantly on the substituents at the phosphorus atom. For this reason, the synthesis of tetra-alkoxydiphosphines, which may be assumed to undergo all the numerous reactions known in the chemistry of trialkyl phosphites, is therefore of special interest. A new approach to the synthesis of tetra-alkoxydiphosphines is based on the employment of dialkoxyphosphines—the full esters of hypophosphorous acid[142,143]. It has been shown that soft bases (dialkoxyphosphines) react with soft acids (dialkyl phosphorochloridites) to form tetra-alkoxydiphosphines[144,145]:

$$(RO)_2PH + (R'O)_2PCl \xrightarrow[90\%]{Et_3N} (RO)_2P-P(OR')_2 + Et_3N\cdot HCl\ .$$

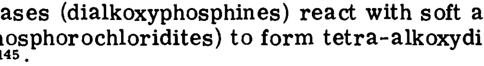
Symmetrical $(RO)_4P_2$ may be obtained (in yields up to 50%) without isolating $(RO)_2PH$:[146]

$$2(RO)_2PCl + R_3SnH \xrightarrow{Et_3N} [(RO)_2PH + (RO)_2PCl] \xrightarrow{Et_3N} (RO)_2P-P(OR)_2 + Et_3N\cdot HCl.$$

The synthesis (via the mechanism described above) of dialkoxydialkyldiphosphines—compounds with two centres of different basicity ("phosphite" and "phosphine")—is also of undoubted interest[14]:

$$(RO)_2PH + R'_2PCl \xrightarrow{R''_3N} (RO)_2P-PR_2 + R''_3N\cdot HCl\ ,$$
$$R_2PH + (R'O)_2PCl \xrightarrow{R''_3N} R_2P-P(OR')_2 + R''_3N\cdot HCl\ .$$

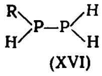
For the given type of interaction, the choice of the pair of reactants is not immaterial: the first reaction gives a yield of 70%, while that of the second is only 45%: dialkylphosphines (particularly when they are sterically hindered) react much more slowly than dialkoxyphosphines. The synthesis of trialkoxyalkyldiphosphines has been described[146]:

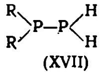


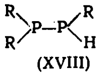
$$(RO)_2PH + R'(RO)PCl \xrightarrow{R''_3N} (RO)_2P-P(OR)R' + R''_3N\cdot HCl\ .$$

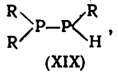
It is noteworthy that asymmetric diphosphines are as a rule difficult to obtain (the yields do not exceed 40%) owing to their disproportionation to symmetrical compounds.

The organic diphosphines (XVII)-(XX) with PH bonds in the molecule

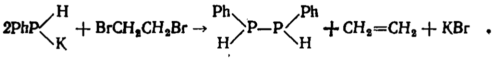

(XVI)


(XVII)


(XVIII)

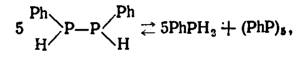

(XIX)

are known only in a few instances. Among di-s-diphosphines [compounds (XIX)], 1,2-bis(trifluoromethyl)diphosphine has been described[129]; it was obtained, among other products, by the cautious hydrolysis of $(CF_3P)_4$. A seemingly general method of synthesis of diphosphines of type (XIX) was proposed in 1971:[132]



$$2PhP(H)K + BrCH_2CH_2Br \rightarrow Ph(H)P-P(H)Ph + CH_2{=}CH_2 + KBr\ .$$

However, the equilibrium



$$5\,Ph(H)P-P(H)Ph \rightleftarrows 5PhPH_2 + (PhP)_5,$$

in which a diphosphine of type (XIX) exists as a distereoisomeric mixture of the *meso*- and *dl*-forms, occurs in the temperature range between 30° and 200°C. The energy of the transition between these forms is 22-24 kcal mole^{-1}, i.e. is of the same order of magnitude as the energy of the given transition for R_4P_2.[82] It has been suggested that the intermediates $Ph\ddot{P}$: occurs in this equilibrium, particularly since the process[147]

$$5(F_3CP)_4 + 20MePH_2 \rightarrow 20F_3CPH_2 + 4(MeP)_5$$

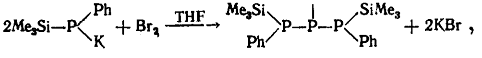
takes place.

Above 225°C, the di-s-diphosphine $(CH_3PH)_2$ is converted into a mixture of $(CF_3P)_n$ and CF_3PH_2, but in contrast to the previous process, the reaction is irreversible[9]. A diphosphine of type (XVIII) is formed from a mixture of difluorodiphosphine or EtP_2 and an excess of PH_3 at −78°C.[148]

P-P bonds are known to be readily cleaved by amines, but the reaction may be displaced in the opposite direction in the case of the low-boiling dimethylamine[23,149]:

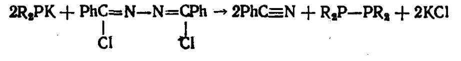
$$(F_3C)_2N-P(CF_3)_2 + Me_2PH \rightarrow Me_2NH + (F_3C)_2P-PMe_2\ ,$$
$$MeP(NMe_2)_2 + 2Ph_2PH \rightarrow MeP(PPh_2)_2 + 2Me_2NH\ ,$$
$$3PhP(NMe_2)_2 + 3PhPH_2 \rightarrow (PhP)_6 + 6Me_2NH\ .$$

Certain non-trivial methods of organic synthesis of diphosphines must also be mentioned. These include the electrochemical method for synthesising Ph_4P_2,[150] the condensation of Ph_2PCl with formation of a P-P bond on treatment with calcium carbide[151,152], and the reduction of di-t-butylmercury by secondary phosphines[153]. Di- and tri-phosphines with P-Si bonds have been obtained from silylated phosphines[154,155]:



$$2Me_3Si-P(Ph)K + Br_2 \xrightarrow{THF} Me_3Si(Ph)P-P(Ph)-P(SiMe_3)Ph + 2KBr\ ,$$
$$2(Me_3Si)_2PLi + BrCH_2CH_2Br \rightarrow (Me_3Si)_2P-P(SiMe_3)_2 + 2LiBr + CH_2{=}CH_2\ .$$

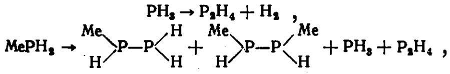
A similar process occurs when lithium and potassium phosphides are acted upon by bis-(α-chlorobenzylidene)-hydrazine[156]:



$$2R_2PK + PhC(Cl){=}N-N{=}C(Cl)Ph \rightarrow 2PhC{\equiv}N + R_2P-PR_2 + 2KCl\ .$$

A new method for the synthesis of thermodynamically unstable organic compounds—in a silent electric discharge at low pressures—has been proposed recently[15]. In the series of OPC this method was used for the first time to synthesise tetrachlorodiphosphine[31] and in recent years also for the synthesis of a number of unstable diphosphines, particularly diphosphines with P-H bonds[158]:

$$PH_3 \rightarrow P_2H_4 + H_2\ ,$$



$$MePH_2 \rightarrow Me(H)P-PH_2 + Me(H)P-P(H)Me + PH_3 + P_2H_4\ ,$$
$$F_3CPH_2 \rightarrow F_3CP(H)-P(H)CF_3 + PH_3 + (F_3C)_2PH + (F_3C)_3P\ .$$

For methyldiphosphine, equilibrium with the cyclic form is established even at room temperature[159]:

$$MeP(H)PH_2 \rightleftarrows MePH_2 + \frac{1}{n}(MeP)_n\ .$$

Diphosphines with P–H bonds can also undergo further disproportionation in a silent discharge[158]:

$$F_3C(H)P{-}P(H)CF_3 \rightarrow F_3CPH_2 + (F_3C)_3P + (F_3C)_4P_2 \ .$$

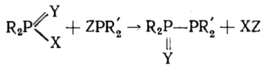
P–P bonds are formed in the thermolysis or photolysis of metal complexes with tertiary or secondary phosphines[160,161]:

$$Fe(CO)_4 \cdot HPR_2 \xrightarrow{h\nu} Fe_2(CO)_6(PR_2)_2 \ ,$$
$$W(CO)_5 \cdot HPR_2 \xrightarrow{\Delta} W_2(CO)_8(PR_2)_2 + W_2 + (CO)_7(PR_2)_2 + R_2PH \ .$$

The presence of a P–P bond in the complexes formed was established by X-ray diffraction. Many of the above complexes cannot be synthesised directly from organic diphosphines (bidentate ligands) and metal carbonyls, since dissociation of P–P bonds is frequently observed in these reactions[161–170].

Compounds with a bond between two phosphorus atoms of different valence may be synthesised by the oxidation of organic diphosphines, i.e. using compounds with P–P bonds already present. These reactions are discussed below and can be used on a preparative scale when the corresponding organic diphosphines are available.

A set of reactions, which may be described in terms of the formal general mechanism



$$R_2P{\overset{\displaystyle /\!\!/ Y}{\underset{\displaystyle \diagdown X}{}}} + ZPR'_2 \rightarrow \underset{\underset{\displaystyle Y}{\|}}{R_2P}{-}PR'_2 + XZ$$

and which give satisfactory yields in certain specific cases, have been suggested for the synthesis of diphosphine monoxides (monosulphides):

$$R_2P(O)H + R'_2PCl \xrightarrow[-HCl]{Et_3N} R_2P(O){-}PR'_2 \ (\text{Ref.}170) \ ,$$
$$R_2P(O)H + R'_2P{-}NMe_2 \xrightarrow{\leftarrow Me_2NH} R_2P(O){-}PR'_2 \ (\text{Ref.}99) \ ,$$
$$R_2PONa + R'_2PCl \xrightarrow{-NaCl} R_2P(O){-}PR_2 \ (\text{Refs. } 172{,}173) \ .$$

The interaction with dialkylphosphinous acids is complicated by the exchange reaction[174]:

$$R_2P(O)H + R'_2PCl \rightleftarrows R_2PCl + R'_2P(O)H \ ,$$

which may be suppressed by an excess of a tertiary amine. The attack by dialkylchlorophosphine on the two basic centres of the ambident anion $R_2P{-}S^-$ proceeds in the same way as on the $R_2P{-}O^-$ anion—mainly on the phosphorus atom[174]:

$$R_2PSNa + R_2PCl \xrightarrow{-NaCl} \underset{95\%}{R_2P(S){-}PR_2} + \underset{5\%}{R_2P{-}S{-}PR_2} \ .$$

In the presence of primary substituents, monosulphides are formed exclusively; they are stable and do not rearrange to thioanhydrides. In the presence of tertiary substituents it is impossible to detect the corresponding monosulphide: only thioanhydrides of phosphinous acids are always isolated, which may be a consequence of thermodynamic control, i.e. a result of the rapid rearrangement of the monosulphide to the thioanhydride. In the presence of secondary substituents, a tautomeric mixture of the corresponding monosulphides and thioanhydrides is formed. Problems associated with the rearrangement in this series will be discussed in greater detail below.

Dialkoxydialkyldiphosphine monoxides are formed in virtually quantitative yields as a result of the exothermic reaction[175]

$$R_2PONa + ClP(OR)_2 \rightarrow R_2P(O){-}P(OR)_2 \ .$$

It makes it possible to obtain 2,2-dialkoxy-1,1-dialkyl-1-oxodiphosphines; the second isomer of the monoxide—2,2-dialkoxy-1,1-dialkyl-2-oxodiphosphine—is formed from dialkylchlorophosphines and dialkyl phosphites:

$$(RO)_2P(O)H + R'_2PCl \xrightarrow{Et_3N} R'_2P{-}(O)P(OR)_2 \ ,$$

and also from tetra-alkylpyrophosphites[175]:

$$(R'O)_2P{-}O{-}P(OR')_2 + R_2PCl \xrightarrow{R'_3N} R_2P{-}(O)P(OR')_2 + (R'O)_2PCl \ :$$

The monosulphides are also readily obtainable[176]:

$$R_2P(S)H + (RO)_2PCl \xrightarrow{R_3N} R_2P(S){-}P(OR)_2 \ .$$

It is noteworthy, that dialkylphosphinous acids give rise only to mixed anhydrides of phosphonous and phosphorous acids in this reaction. 2,2-Dialkoxy-1,1-dialkyl-2-thionodiphosphines can be synthesised from the 1-sulphides[176]:

$$R_2P(S){-}P(OR)_2 \xrightarrow{\Delta} R_2P{-}P(S)(OR)_2 \ .$$

Tetra-alkoxydiphosphine monoxides are stable for several hours, while tetra-alkoxydiphosphine monosulphides are entirely stable and can be formed via a similar mechanism[177,178]:

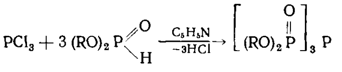
$$(RO)_2PXNa + (R'O)_2PCl \rightarrow (RO)_2P(X){-}P(OR')_2 + NaCl \ ,$$

where X = S or O.

The interaction of diphenylphosphine oxide with the mixed anhydride of acetic and diphenylphosphinous acids may be regarded as a variant of the above reactions[177]:

$$Ph_2P(O)H \xrightarrow{(MeCO)_2O} Ph_2PO(O)CMe \xrightarrow[-MeCOOH]{Ph_2P(O)H} Ph_2P(O){-}PPh_2 \ .$$

Using this scheme, it is possible to obtain compounds with three P–P bonds in the molecule in 63% yields[178]:



$$PCl_3 + 3\,(RO)_2P{\overset{\displaystyle /\!\!/ O}{\underset{\displaystyle \diagdown H}{}}} \xrightarrow[-3HCl]{C_5H_5N} \left[(RO)_2\overset{\overset{\displaystyle O}{\|}}{P}\right]_3 P \ .$$

The biphilic properties of compounds with a three-coordinated phosphorus atom suggest yet another method for the formation of a P–P bond between phosphorus atoms with different coordination [numbers?]. Indeed highly nucleophilic soft bases (trialkylphosphines, dialkylphosphines, or aminophosphines) react with electrophilic soft acids (dialkylchlorophosphines) to form crystalline adducts in which a P–P bond is formed according to NMR spectroscopic data[138,179–182]:

$$Me_3P + ClPR_2 \rightarrow [Me_3P{-}PR_2]^+Cl^- \ ,$$
$$R_2PH + R_2PCl \rightarrow [R_2P{-}P(H)R_2]^+Cl^- \ ,$$
$$R_3P{=}NPR'_2 + R''_2PCl \rightarrow [R_3P{=}N{-}P(R'_2){-}PR''_2]^+Cl^- \ .$$

The reaction is appreciably reversible in solution in methylene chloride and does not occur for weakly nucleophilic tertiary phosphines, for example, $MePh_2P$. However, the latter reacts with the more electrophilic chloride PCl_3 to form the corresponding adduct at 20°C. The adducts are usually stable up to room temperature. When two moles of dialkylchlorophosphines are used, the tertiary phosphine behaves as a "condensing" agent and tetra-alkyldiphosphines are formed in satisfactory yields[138,179,183].

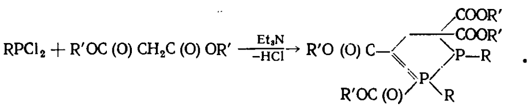
If esters of phosphonous, phosphinous, and phosphorous acids are used instead of tertiary phosphines, the Arbuzov rearrangement may occur in the system via intermediates of the type described above, which apparently have the structure of quasi-phosphonium compounds with P–P bonds[184–186]:

$$Ph_2POR + Ph_2PCl \rightarrow Ph_2P{-}P(O)Ph_2 + RCl \ ,$$
$$MeP(OMe)_2 + Ph_2PCl \rightarrow [Ph_2P{-}P(OMe)_2Me]^+Cl^- \rightarrow Ph_2P(O)(OMe)Me + MeCl \ ,$$
$$(RO)_3P + Ph_2PCl \rightarrow [(RO)_3P \rightarrow P(Cl)Ph_2] \rightarrow (RO)_2P(O){-}PPh_2 + RCl \ ,$$
$$(RO)_3P + PhPCl_2 \rightarrow PhP(Cl){-}P(O)(OR)_2 + RCl \ .$$

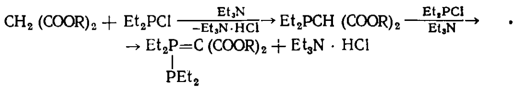
The addition of a second equivalent of chlorophosphine leads to the dissociation of the P–P bond in the resulting monoxide; thus diphosphines may be obtained in satisfactory yields for a 1 : 2 reactant ratio[184]:

$$\text{MeP(OMe)}_2 + \text{Ph}_2\text{PCl} \rightarrow \text{MeP(O)(OMe)—PPh}_2 \xrightarrow{\text{Ph}_2\text{PCl}} \text{Ph}_2\text{P—PPh}_2 + \text{Me(MeO)P(O)Cl} .$$

Ylids of a new type with a P–P bond between three- and four-coordinated phosphorus atoms have been obtained from malonic ester and a wide variety of alkyl(aryl)dichlorophosphines[187]:



Similar phosphoranes but with a linear structure are formed from malonic esters and Et_2PCl:[188]



$$\text{CH}_2(\text{COOR})_2 + \text{Et}_2\text{PCl} \xrightarrow[-\text{Et}_3\text{N}\cdot\text{HCl}]{\text{Et}_3\text{N}} \text{Et}_2\text{PCH(COOR)}_2 \xrightarrow[\text{Et}_3\text{N}]{\text{Et}_2\text{PCl}} \rightarrow \underset{\substack{|\\ \text{PEt}_2}}{\text{Et}_2\text{P}}\text{=C(COOR)}_2 + \text{Et}_3\text{N}\cdot\text{HCl} .$$

The methods of synthesis of OPC with P–P bonds are closely interrelated with certain reactions of organic diphosphines, which lead to new OPC, also with P–P bonds. Part of the synthetic data will therefore be found in the next section of this review.

IV. THE REACTIVITIES OF COMPOUNDS WITH P–P BONDS

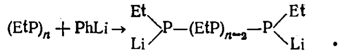
The idea of the biphilic nature of OPC with a three-coordinated phosphorus atom is widely used in phosphorus chemistry. It can be extended to organic diphosphines, which exhibit a high reactivity in relation to both nucleophiles and electrophiles; the P–P bond is then most "vulnerable". Numerous reactions involving the dissociation of P–P bonds are known and many of these may be said to involve the heterolytic dissociation of P–P bonds, although even indirect confirmation of the reaction mechanism is by no means always presented.

The P–P bond in organic diphosphines and cyclopolyphosphines is readily cleaved by nucleophiles such as alkali metals[115,189,190], the ease of dissociation depending both on the substituents at the phosphorus atoms and on the alkali metal (K > Na > Li). Tetraphenyldiphosphine is more reactive in relation to sodium than tetra-alkyldiphosphines, which may be accounted for by the greater stability of the Ph_2P^- anion formed compared with R_2P^-. Typical nucleophiles (organolithium compounds) also dissociate P–P bonds[118,191]:

$$\text{R}_2\text{P—PR}_2 + \text{PhLi} \rightarrow \text{R}_2\text{PLi} + \text{R}_2\text{PPh} .$$

The reactivity of organic diphosphines in this interaction (for example, in relation to PhLi) is consistent with the ideas concerning the mechanism of bimolecular nucleophilic substitution at a phosphorus atom. Thus the reactivity decreases in the sequence Ph > Me > Et > n-Pr > n-Bu. The reaction results in the formation of new anion R_2P^-, the stability of which (and hence the ease of its elimination) decreases with increase of the *–I* effect of the substituents. Steric factors also play a significant role in this reaction: it does not occur at all for R = iso-Pr, t-Bu, or cyclo-C_6H_{11}.

Cyclopolyphosphines are also cleaved by organolithium compounds[118,192,193]. The reaction consists of many stages, a product resulting from the dissociation of one P–P bond being formed initially:

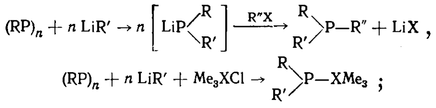


$$(\text{EtP})_n + \text{PhLi} \rightarrow (\text{Et})(\text{Li})\text{P—(EtP)}_{n-2}\text{—P}(\text{Et})(\text{Li}) .$$

The product then reacts rapidly with phenyl-lithium to form secondary cleavage products: $EtP(Li)(PEt)_2P(Li)Et$ and Et_4P_2. The final products are lithium di- and mono-alkylphosphides and ethyldiphenylphosphine.

A detailed study of the interaction of Ph_4P_2 with phenyl-lithium[192,193] made it possible to establish the following electrophilicity series in relation to phenyl-lithium: $Li(PPh)_{n-1}PPh_2 (n \geqslant 3) > (PhP)_n (n = 3 - 5) > Li(PPh)_4Li > Ph_2P{-}PPh_2,\ Li(PPh)_3Li > (Ph)(Li)P{-}PPh_2 > Li(PPh)_2Li$.

The cleavage of P–P bonds in cyclopolyphosphines is used to synthesise linear polyphosphines (as was considered in the previous section). In addition, the availability and high reactivity of cyclopolyphosphines made it possible to develop on their basis a general method for the synthesis of chiral tertiary phosphines and also compounds with P–Ge, P–Si, and P–Sn bonds[194]:



$$(\text{RP})_n + n\,\text{LiR}' \rightarrow n\left[\text{LiP}(\text{R})(\text{R}')\right] \xrightarrow{\text{R}''\text{X}} (\text{R})(\text{R}')\text{P—R}'' + \text{LiX} ,$$

$$(\text{RP})_n + n\,\text{LiR}' + \text{Me}_3\text{XCl} \rightarrow (\text{R})(\text{R}')\text{P—XMe}_3 ;$$

X=Si, Ge, or Sn.

The interaction of organic diphosphines with alkali metal phosphides, the nucleophilic properties of which are weaker than those of organolithium compounds, takes place more slowly[193]:

$$\text{Ph}_2\text{P—PPh}_2 + \text{LiPR}_2 \rightarrow \text{Ph}_2\text{P—PR}_2 + \text{LiPPh}_2 ,$$
$$\text{Ph}_2\text{P—PR}_2 + \text{LiPR}_2 \rightarrow \text{R}_2\text{P—PR}_2 + \text{LiPPh}_2 ,$$

and may be stopped at the first stage. In the second stage attack by the R_2P^- anion is directed to the most nucleophilic centre in the molecule, which is probably associated with the ease of formation of the Ph_2P^- anion.

Cyclic polyphosphines are cleaved only by the more reactive Li_2PPh; the yield of the reactions with monolithium phosphides does not exceed 2–3%.[189–193]

Depending on the nature of the substituents at the phosphorus atom, the reactivity of organic diphosphines in relation to nucleophiles may be altered sharply: electron-accepting substituents promote the cleavage of the P–P bond. Thus water does not react at all with tetra-alkyldiphosphines[3], but reacts rigorously with tetra-alkoxydiphosphines[130]:

$$(\text{RO})_2\text{P—P(OR)}_2 + \text{H}_2\text{O} \rightarrow (\text{RO})_2\text{PH} + (\text{RO})_2\text{P(O)H} .$$

In the cold it causes quantitative dissociation of the P–P bond in diphosphines with electron-accepting substituents[3,63,179]:

$$\text{F}_2\text{P—PF}_2 + \text{H}_2\text{O} \rightarrow \text{F}_2\text{PH} + \text{F}_2\text{P—O—PF}_2 ,$$
$$\text{Me}_2\text{P—P(CF}_3)_2 + \text{H}_2\text{O} \rightarrow \text{Me}_2\text{P(O)H} + (\text{CF}_3)_2\text{PH} .$$

The reaction is accelerated sharply in the presence of an inorganic acid: the formation of $(CF_3)_2PH$ and $Me_2P(O)H$, and not $(CF_3)_2P(O)H$ and Me_2PH, as a result of the reaction may be accounted for by the initial protonation of the Me_2P group by traces of acid, the presence of which could not be as a rule avoided owing to the method used to synthesise dimethyldi(trifluoromethyl)diphosphine, and subsequent nucleophilic attack by water molecules on the phosphonium centre.

Owing to the high reactivity of the P–Cl and P–I bonds, tetraiodo- and tetrachloro-diphosphines form further hydrolysis products with dissociation of the P–P bond[195-197].

There are comparatively few data on the alcoholysis of organic diphosphines. 1,2-Dibromo-1,2-bis(trichloromethyl)diphosphine reacts with ethanol even at low temperatures to form diethyl trichloromethylphosphonite[129]. Tetra-alkoxydiphosphines undergo quantitative exothermic cleavage by ethanol[130].

Like tetra-alkyldiphosphines, cyclopolyphosphines are resistant to neutral hydrolysis but are readily cleaved by aqueous alkali: the P–C and P–P bonds in $(CF_3P)_4$ and $(CF_3P)_5$ dissociate with formation of CF_3H, H_2, and CF_3PH_2. The process is appreciably accelerated in diglyme and at low temperatures the interaction with water and alcohol leads to di-, tri-, and tetra-phosphines with linear structures[198]:

$$\begin{gathered}(F_3CP)_5 + H_2O \rightarrow H(CF_3)P{-}P(CF_3)H + F_3C(H)P{-}P(CF_3)P(H)CF_3 + \\ + H(F_3C)P(PCF_3)_2{-}P(H)CF_3 \\ (F_3CP)_4 + MeOH \rightarrow F_3C(H)P{-}P(CF_3)OMe + F_3C(H)P{-}P(H)CF_3 + \\ + (F_3C)_2POMe + H(F_3C)P{-}\underset{\underset{CF_3}{|}}{P}{-}P(CF_3)H \quad .\end{gathered}$$

The mechanism of the homolytic cleavage of the P–P bond has been discussed[199]. Isolated instances where alcoholysis goes to completion without the dissociation of the P–P bond have been reported[140].

Ammonia is relatively unreactive in relation to $(CF_3)_4P_2$: only 48% of the latter reacts after 28 days at 20° C. Chloramine proved to be somewhat more reactive in this process[200]:

$$R_2P{-}PR_2 + NH_2Cl \rightarrow R_2PCl + R_2PNH_2 \quad .$$

Secondary amines do not dissociate the P–P bond in di-iododiphosphines at 20° C, since under these conditions the reactivities of the P–P and P–I bonds apparently become comparable[131]. However, the P–P bond dissociates even on boiling in ether[201]:

$$PhP(I){-}P(I)Ph + 3HN(CH_2)_5 \rightarrow (PhP)_n + PhP[N(CH_2)_5]_2 + 2(CH_2)_5NH_2I \quad .$$

Nucleophilic attack on asymmetric alkoxydialkyldiphosphines is directed to the most electrophilic phosphite centre in the molecule[202]:

$$(\text{iso-Pr})_2P{-}P(OBu)_2 + PhNHEt \rightarrow (\text{iso-Pr})_2NH + (BuO)_2PN(Et)Ph \quad .$$

Since the less basic diphenylamine reacts much more slowly and piperidine does not react at all, the hypothesis of an optimum ratio of the nucleophilicity of the amine and its capacity for electrophilic cooperation (i.e. its acidity), whereupon the process proceeds at the maximum rate, appears to be very well-founded. The equilibrium in the reactions of tetra-alkyldiphosphines, whose electrophilic properties are fairly weak, with amines is known to be displaced in the opposite direction[3]:

$$EtPNMe_2 + R_2PH \rightarrow Et_2P{-}PR_2 + Me_2NH \quad .$$

The interaction with stronger nucleophiles (secondary phosphines) takes place non-selectively, simultaneously at the phosphite and phosphine centres[202]:

$$\begin{gathered}(\text{iso-Pr})_2P{-}P(OBu)_2 + Ph_2PH \rightarrow (\text{iso-Pr})_2P{-}PPh_2 + \\ + (BuO)_2PH + Ph_2P{-}P(OBu)_2 + (\text{iso-Pr})_2PH \\ \xrightarrow{Ph_2PH} Ph_2P{-}PPh_2 + (BuO)_2PH \quad .\end{gathered}$$

Organic diphosphines (at least those with one highly electrophilic centre) react with tertiary phosphines to form complexes—for example, the complex $(CF_3)_2P\text{-}PMe_2.Me_3P$. Secondary phosphines and arsines dissociate the P–P bond only in $(CF_3)_4P_2$:[149]

$$(CF_3)_2P{-}P(CF_3)_2 + Me_2XH \rightarrow (CF_3)_2P{-}XMe_2 + (CF_3)_2PH \ ; \quad X = \text{P or As.}$$

As described above, the P–P bond in the cyclic analogue $(CF_3)_4P_4$ is broken quantitatively under the influence of primary phosphines even at room temperature[147,203].

Organic diphosphine monoxides are much more resistant to nucleophiles than the diphosphines themselves. Thus tetra-isopropyldiphosphine monoxide requires a week for its hydrolysis by water at 20° C; the reaction with alcohol is just as slow[174]:

$$\begin{gathered}(\text{iso-Pr})_2P(O){-}P(\text{Pr-iso})_2 + H_2O \rightarrow 2\ (\text{iso-Pr})_2P(O)H \ ; \\ (\text{iso-Pr})_2P(O){-}P(\text{Pr-iso})_2 + EtOH \rightarrow (\text{iso-Pr})_2P(O)H + (\text{iso-Pr})_2POEt \ .\end{gathered}$$

The monoxides do not react with diethylamine even on heating.

Organotin hydrides, in which the amount of ionic character of the Sn–H bond is greater than in the Si–H and Ge–H bonds, cleave the P–P bond in the most electrophilic organic diphosphines at 20° C:[204]

$$\begin{gathered}(F_3C)_2P{-}P(CF_3)_2 + Me_3SnH \xrightarrow{20^\circ} Me_3Sn{-}P(CF_3)_2 + HPMe_2 \ , \\ (F_3CP)_4 + Me_3SnH \xrightarrow{20^\circ} Me_3Sn{-}P(CF_3)H + (Me_3Sn)_2PCF_3 + H_2PCF_3 \ , \\ (F_3C)_2P{-}PH_2 + R_3SnH \rightarrow R_3Sn{-}P(CF_3)_2 + PH_3 \quad .\end{gathered}$$

Trimethylgermane reacts very slowly only at 150° C and the corresponding silicon hydrides do not react even at this temperature. Under the conditions of radical interaction, it is possible to achieve the reaction also with trimethylsilane:

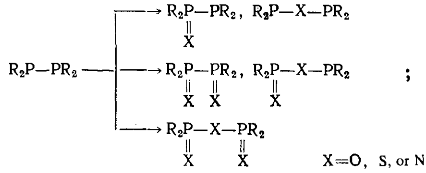
$$(F_3C)_2P{-}P(CF_3)_2 + HSiMe_3 \xrightarrow{h\nu} Me_3Si{-}P(CF_3)_2 + HP(CF_3)_2 \ .$$

Protic acids HX in aqueous media readily cleave the P–P bond[205,206]. In the presence of electron-accepting substituents at the phosphorus atom the reactivity of the compounds in reactions with protic acids is greatly reduced. Thus Ph_4P_2 reacts with hydrochloric acid more vigorously than the asymmetric dimethyldi(trifluoromethyl)-diphosphine: anhydrous protic acids do not react with $(CF_3)_4P_2$ and the reaction with $(CF_3P)_n$ (n = 4 or 5) takes place only after prolonged heating (up to 100° C in the case of sulphuric acid).[207] Carboxylic acids cleave the P–P bond in Ph_4P_2 under very severe conditions (150°–200° C) and the process is complicated by many side reactions[208]. The ability of the P–P bond to be cleaved by acids has been used in the elimination of diphosphines from phosphines[209].

The reduction of aromatic diphosphines at carbon or mercury electrodes involves the dissociation of the P–P bond[210,211]. Their reduction by $LiAlH_4$ also takes place with dissociation of the P–P bond.[212]

Being typical nucleophiles, organic diphosphines form, like tertiary phosphines, stable complexes with Lewis acids[213,214]. Thus Ph_4P_2 forms a complex with a single molecule of trialkylaluminium. The more nucleophilic Me_4P_2 forms a complex with two triethylaluminium molecules[213]. Like tertiary phosphines, Et_4P_2 forms a stable 1 : 1 complex with CuBr.[215,216]

Like tertiary phosphines, organic di- and poly-phosphines are extremely sensitive to oxidation. On oxidation, there is a possibility of the formation of the following structures:



X=O, S, or NR.

It has been shown[151,152] that the result of the oxidation of Ph_4P_2 depends on the purity of the test specimen. In all other cases only the structure of the final product was deduced as a rule:

$$P_2F_4 + O_2 \rightarrow F_2P{-}O{-}PF_2, \text{(Ref.129)}$$

$$Alk_2P{-}PAlk_2 + S \rightarrow Alk_2P{-}P(S)Alk_2 \xrightarrow[(O_2)]{S}$$

$$\rightarrow Alk_2P(S){-}P(S)Alk_2\ [Alk_2P(O){-}P(O)Alk_2], \text{(Refs.134,136,190,217,218)}$$

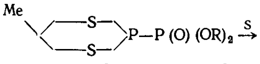
$$(t\text{-}Bu)_2P{-}P(Bu\text{-}t)_2 \xrightarrow{S} (t\text{-}Bu)_2P(S){-}P(Bu\text{-}t)_2 \rightarrow$$

$$\xrightarrow{S} (t\text{-}Bu)_2P(S){-}S{-}P(S)(Bu\text{-}t)_2, \text{(Refs.134,202)}$$

$$R_2P(O)PR_2 \xrightarrow{O_2(S)} R_2P(O){-}P(O,\ S)R_2, \text{(Ref.98)}$$

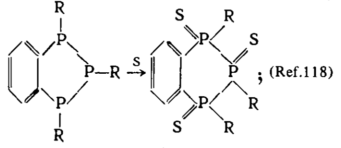
$$(RO)_2P{-}P(OR)_2 \xrightarrow{O_2} (RO)_2P{-}O{-}P(OR)_2, \text{(Ref.220)}$$

$$(RO)_2P{-}P(OR)_2 \xrightarrow{S} (RO)_2P(S){-}P(S)(OR)_2, \text{(Ref.221)}$$


$\xrightarrow{S}$ reaction does not proceed (Ref.219),

$$I_2P{-}PI_2 \xrightarrow{Se} I_2P(Se){-}PI_2 \xrightarrow{Se} I_2P(Se){-}P(Se)I_2, \text{(Ref.118)}$$

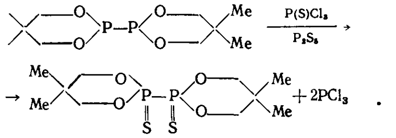
$$Ph_2P{-}P(Me){-}PPh_2 \xrightarrow{S} Ph_2P(S){-}P(Me){-}P(S)Ph_2, \text{(Ref.202)}$$


; (Ref.118)

R=Et, or Ph.

Apart from oxygen, a large number of oxidants have been used to oxidise organic diphosphines. In particular, it has been shown that diphosphine disulphides[202], $PSCl_3$, and P_2S_5[140] may be oxidised:

$$Me(Et)P{-}P(Et)Me + Me(Et)P(S){-}P(S)(Et)Me \xrightarrow[15\ h]{190^\circ} 2Me(Et)P{-}P(S)(Et)Me\ ,$$



The oxidation of tetra-alkoxydiphosphines by nitric oxide and pyridine *N*-oxide results in the formation of a mixture of products containing compounds with a single phosphorus atom and tetra-alkyl pyrophosphites. The use of dimethyl sulphoxide (DMSO) in the oxidation of tetra-alkoxydiphosphines is preparatively convenient[221]:

$$(RO)_2P{-}P(OR)_2 + Me_2S{=}O \left| \begin{array}{l} \xrightarrow{1:1} (RO)_2P{-}O{-}P(OR)_2 + Me_2S \\ \xrightarrow{1:2} (RO)_2P(O){-}O{-}P(OR)_2 + 2Me_2S \\ \xrightarrow{1:3} (RO)_2P(O){-}O{-}P(O)(OR)_2 + 3Me_2S\ . \end{array} \right.$$

It is logical to treat this reaction as one involving electrophilic attack by one of the phosphorus atoms on the oxygen atom in the DMSO molecule with subsequent rearrangement of the intermediate tetra-alkoxydiphosphine monoxide. Such rearrangement has been postulated in the study of the alkylation of tetra-alkoxydiphosphines[221] and its occurrence has been demonstrated[173]. It has been shown that tetra-alkyl pyrophosphite is a secondary product of the reaction of dialkyl phosphorochloridites with dialkyl phosphite salts and that the monoxide formed initially is stable for several hours.

In the absence of a solvent, the interaction of tetra-alkoxydiphosphines with DMSO proceeds in a different manner[221]:

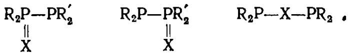
$$(RO)_2P{-}P(OR)_2 + 2Me_2S{=}O \rightarrow (RO)_2P(O)CH_2SMe + (RO)_2P(O)H + Me_2S\ .$$

It appears that a definite analogy may be drawn between data for the above interaction and the reaction of DMSO with acetic anhydride (the Pummerer reaction).[222]

The oxidation of tetra-alkyldiphosphines to the corresponding *P*-imines by trimethylsilyl azide proceeds in stages[207,223]:

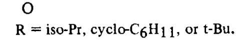
$$R_2P{-}PR_2 \xrightarrow[-N_2]{Me_3SiN_3} R_2P(=NSiMe_3){-}PR_2 \xrightarrow[-N_2]{Me_3SiN_3} R_2P(=NSiMe_3){-}P(=NSiMe_3)R_2\ .$$

The existence of three isomeric structures of the monoxides of asymmetric organic diphosphines was already mentioned above:



$$\underset{\substack{\| \\ X}}{R_2P}{-}PR'_2 \qquad R_2P{-}\underset{\substack{\| \\ X}}{PR'_2} \qquad R_2P{-}X{-}PR_2\ .$$

The problem of the conditions governing the formation and stability of these structures is of independent significance and its detailed elucidation made it possible to discover new rearrangements and the previously unknown phenomenon of non-prototropic tautomerism of OPC[224,225]. Thus it has been found that irreversible rearrangements take place in the following series of compounds[172]:



$$\underset{\substack{\| \\ O}}{Ph_2P}{-}PR_2 \rightarrow Ph_2P{-}P(O)R_2\ ;$$

R = iso-Pr, cyclo-C_6H_{11}, or t-Bu.

The rate of rearrangement depends on the nature of the alkyl substituent and increases in the presence of a catalyst and on heating. For R = cyclo-C_6H_{11}, the rearrangement is completed in five weeks at room temperature and in 4 h at 80° C in the presence of $MgBr_2$. Tetra-alkyldiphosphine monoxides rearrange under more severe conditions[172]:

$$Bu_2P(O){-}P(Bu\text{-}t)_2 \xrightarrow[190-200^\circ,\ 3-4\ h]{MgBr_2} (t\text{-}Bu)_2P(O){-}PBu_2\ .$$

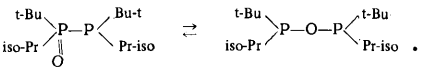
These data show that the thermodynamic stability of the isomeric monoxides of asymmetric diphosphines is determined by the nature of the substituent.

The existence of dialkylphosphinous acid anhydrides is limited by the very narrow range of suitable alkyl substituents, which is evidently associated with the steric and not electronic influence of the substituents[174,225]:

$$R_2P(O){-}PR_2 \xrightarrow[180^\circ]{MgBr_2} R_2P{-}O{-}PR_2\ ;$$

R = t-Bu.

Non-prototropic tautomerism has been observed in the following reaction[174] (we may note that the content of the anhydride increases appreciably with increase of temperature):



The accumulation of bulky substituents at the phosphorus atoms destabilises the monoxide to such an extent that its thermodynamic stability becomes comparable to that of the anhydride, since the stability of a compound with the P-O-P fragment should be less influenced by steric hindrance. Tetra-(t-butyl)diphosphine monoxide rearranges irreversibly to the anhydride of di-(t-butyl)phosphinous acid, as mentioned above.

Tetra-alkyldiphosphine monosulphides are entirely stable and usually do not rearrange on heating and under the influence of catalysts. An irreversible rearrangement occurs only for tetrahalogenodiphosphine monosulphides[117,226]:

$$F_2P(S){-}PF_2 \rightarrow F_2P{-}S{-}PF_2\ ,$$

$$I_2P(Se){-}PI_2 \rightarrow I_2P{-}Se{-}PI_2\ .$$

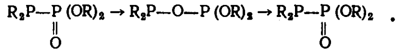
The rearrangement of tetra-alkyldiphosphine monosulphides[174] with secondary substituents is reversible:

$$(iso\text{-}Pr_2\ P(S){-}P(Pr\text{-}\mathit{изо})_2 \rightleftarrows (iso\text{-}Pr)_2P{-}S{-}P(Pr\text{-}iso)_2.$$

An unusual pathway in the oxidation of organic diphosphines containing phosphorus atoms of different basicities has been discovered, namely the oxidation of the less basic phosphite centre in 2,2-dibutoxy-1,1-di-isopropyldiphosphine[227,228]:

$$\text{(iso-Pr)}_2\text{P—P(OBu)}_2 + \text{HgO} \rightarrow \text{(iso-Pr)}_2\text{P—P(O)(OBu)}_2 + \text{Hg},$$
$$\text{(t-Bu)}_2\text{P—P(OBu)}_2 + \text{O=IPh} \rightarrow \text{(t-Bu)}_2\text{P—P(O)(OBu)}_2\text{PhI}.$$

In the oxidation of iodosobenzene the monoxide is formed as a result of the kinetic control of the reaction. The oxidation with mercury(II) oxide involves the following rearrangement, the general characteristics of which have been established recently[173,175]:



$$\underset{\text{(XX)}}{\text{R}_2\text{P—}\underset{\underset{\text{O}}{\|}}{\text{P}}\text{(OR)}_2} \rightarrow \underset{\text{(XXI)}}{\text{R}_2\text{P—O—P(OR)}_2} \rightarrow \underset{\text{(XXII)}}{\text{R}_2\text{P—}\underset{\underset{\text{O}}{\|}}{\text{P}}\text{(OR)}_2}.$$

(XX) (XXI) (XXII)

The monoxides (XXII) are thermodynamically the most stable in the series (XX)-(XXII) and represent the final products of the reactions in various systems containing the R_2P and $(R'O)_2P$ fragments and the oxygen atom in proportions of 1 : 1 : 1. The isomerisation of the monoxide (XX) to the mixed anhydride (XXI) may be induced both by phosphorus-containing electrophiles (above −20°C such catalytic isomerisation proceeds in the course of several minutes) and by nucleophiles, which are somewhat less effective. The rearrangement of the anhydride proceeds under more severe conditions[175]:

$$\text{(t-Bu)}_2\text{POP(OBu)}_2 \xrightarrow[120°,\ 3\text{ h}]{\text{HgBr}_2} \text{(t-Bu)}_2\text{P-P(O)(OBu)}_2.$$

As stated above, tetra-ethoxydiphosphine monoxide is stable only for several hours and readily rearranges to the pyrophosphite[176]. On the other hand, tetra-alkoxydiphosphine monosulphides are stable[176], in agreement with data for the oxidation of tetra-alkoxydiphosphine by sulphur[146]:

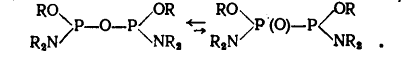
$$\text{(RO)}_2\text{P—P(OR)}_2 \xrightarrow{2\text{S}} \text{(RO)}_2\text{P(S)—P(S)(OR)}_2.$$

The same series of rearrangements is also characteristic of aminodiphosphines[225,229]:

$$\text{R}_2\text{P(O)—P(NR}'_2)_2 \rightarrow \text{R}_2\text{P—O—P(NR}'_2)_2 \rightarrow \text{R}_2\text{P—P(O)(NR}_2)_2.$$

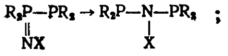
The stability of the monoxide depends apparently on the extent to which the groups linked to the four-coordinated phosphorus atom can participate in the delocalisation of its partial positive charge, i.e. depends on the ratio of the inductive electron-accepting and mesomeric electron-donating properties of the substituents. This is why equilibria in the above reactions are displaced in the opposite directions:

$$\text{(Et}_2\text{N)}_2\text{P—O—P(NEt}_2)_2 \rightleftarrows \text{(Et}_2\text{N)}_2\text{P(O)—P(NEt}_2)_2,$$



The latter equilibrium is strongly displaced to the left, which can be accounted for by the ability of the alkoxy-groups, linked directly to the four-coordinated phosphorus atom, to participate effectively in the delocalisation of the charge on the phosphorus. This is also indicated by the irreversible rearrangement of R_2P-O-$P(OR)_2$ to R_2P-$P(O)(OR)_2$ and not $R_2P(O)P(OR)_2$.[173]

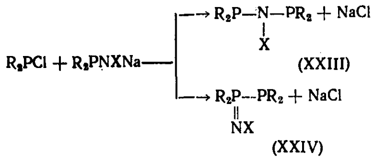
Related rearrangements have been observed also for *P*-imines[230]:



$$\text{R}_2\underset{\underset{\text{NX}}{\|}}{\text{P}}\text{—PR}_2 \rightarrow \text{R}_2\text{P—}\underset{\underset{\text{X}}{|}}{\text{N}}\text{—PR}_2;$$

R = iso-Pr; X = *m*-YC_6H_4, where Y = H, OMe, Cl, Br, or CF_3.

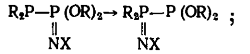
This necessitates a re-examination of the problem of the structure of the products formed initially in the condensation of dialkylchlorophines with an amide salt[231,232]:



(XXIII)

(XXIV)

Dialkoxydialkyldiphosphine imines undergo a slow reaction, which is the opposite of the analogous rearrangement of the monoxides and monosulphides[230]:

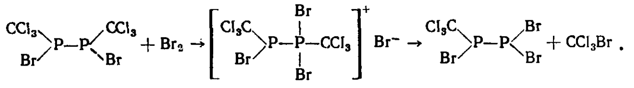


$$\text{R}_2\text{P—}\underset{\underset{\text{NX}}{\|}}{\text{P}}\text{(OR)}_2 \rightarrow \text{R}_2\underset{\underset{\text{NX}}{\|}}{\text{P}}\text{—P(OR)}_2;$$

R = Et, X = NPh .

Cyclic polyphosphines are on the whole more resistant to oxidation than linear polyphosphines, although their reactivity also varies within wide limits. Thus $(CF_3P)_4$ and $(MeP)_4$ ignite in air[134-137], while 1,2,3-triphenyl-1,2,3-triphosphaindan is not oxidised by air in boiling toluene and alcohol[25]. Thus phenyl substituents increase sharply the resistance of the ring to oxidation and the result of the reaction of such compounds depends on the ring size[161-163]. For example, after being refluxed for 2 h in acetonitrile, $(PhP)_6$ does not react with sulphur and nickel tetracarbonyl, while the pentamer is cleaved by sulphur with formation of $(C_6H_5PS)_3$ and behaves as a ligand in relation to $Ni(CO)_4$.

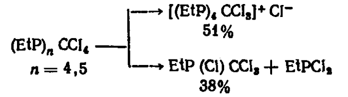
Examination of the oxidation reactions shows that organic diphosphines are extremely reactive nucleophiles. Thus their interaction with both halogens and other halogenating reagents proceeds with dissociation of the P-P bond. It may be that a quasi-phosphonium compound is formed as an intermediate, decomposing subsequently with attack by the anion either on the phosphorus atom or on the carbon atom. In the presence of strongly electronegative substituents the carbon atom is attacked under these conditions, and the P-P bond may be actually retained[111]:



Under more severe conditions, the P-P bond is cleaved even by carbon tetrachloride[234]:

$$\text{R}_2\text{P—PR}_2 + \text{CCl}_4 \underset{\text{C}_n\text{H}_{2n+2}}{\overset{\text{acetonitrile},\ 120\text{–}140°,\ 5\text{ h}}{\rightleftarrows}} \text{R}_2\text{PCl} + \text{R}_2\text{PCCl}_3.$$

The rate of reaction depends to a considerable degree on the substituents at the phosphorus atom; for example, for R = cyclo-C_6H_{11}, heating in the course of 48 h is required and the reverse reaction takes place at 180°C in solution in a hydrocarbon. If the basicity of the diphosphine is enhanced, it is possible to isolate intermediate phosphonium salts of two types: $[Me_2P-P(Me_2)(CCl_2)]^+2Cl^-$ and $[Et_2P-P(Et_2)(CCl_3)]^+Cl^-$ and in the case of cyclopentaphosphines they may be entirely stable[234]:



$$\text{(t-BuP)}_4 \xrightarrow{\text{CCl}_4} \text{reaction does not occur.}$$

In two component primary or secondary amine–carbon tetrachloride systems the interaction is of the type of the Todd–Atherton reaction[235], the yield of the salt increasing in parallel with the enhancement of the nucleophilic properties of the diphosphines and the basicity of the amines.

The reaction involving sterically hindered amines proceeds with formation of a **P–C** bond[236]:

$$(RP)_4 + 2n\,CCl_4 + 4n\,R_2NH \rightarrow n\,[RP(NR_2)_3]^+Cl^- + 2n\,CHCl_3 + n\,[H_2NR_2]^+Cl^-$$
$$R_2P{-}P(O)R_2 + 2CCl_4 + 4HNR_2 \rightarrow [R_2P(NR_2)_2]^+Cl^- + $$
$$+ R_2P(O){-}NR_2 + [R_2NH_2]^+Cl^- + 2CHCl_3\ .$$

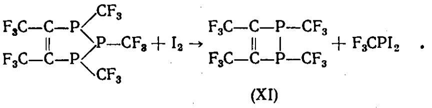
There are instances where the reactions with electrophiles are reversible; the interaction of R_4P_2 with CCl_4 described above is of this kind[202]. Equilibrium of this type may be wholly displaced towards the diphosphine if the halogenating agent is volatile[237]:

$$Cl_3Si{-}SiCl_3 + Me_2PCl \xrightarrow[-SiCl_4]{} Me_2P{-}SiCl_3 \xrightarrow{Me_2PCl} Me_2P{-}PMe_2 + SiCl_4\ .$$

This reaction is also reversible when it involves the dissociation of the low-energy **P–I** bonds[238] and is analogous to the conversion of PI_3 into P_2I_4 in ethereal solution[239]:

$$2ArPI_2 \rightleftarrows ArP(I){-}P(I)Ar + I_2\ .$$

In certain cases [structure **(XI)**] **P–P** bonds are not cleaved at all by iodine[117]:



(XI)

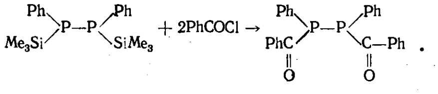
The synthetic possibilities of reactions involving the cleavage of P–P bonds are very extensive. Thus the use in this reaction of carboxylic acid chlorides made it possible to achieve for the first time the synthesis of α-ketophosphonites[240,241]; phosphorus acid chlorides have been used in the synthesis of certain asymmetric dialkoxydialkyldiphosphines[147]:

$$(RO)_2P{-}P(OR)_2 + R'{-}C(O)Cl \rightarrow (RO)_2PC(O)R' + (RO)_2PCl\ ,$$
$$(iso\text{-}Pr)_2P{-}P(OBu)_2 + (PhO)_2PCl \rightarrow (BuO)_2PCl + (iso\text{-}Pr)_2P{-}P(OPh)_2\ .$$

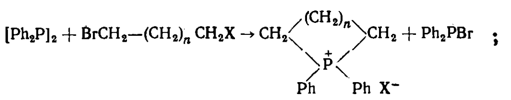
The latter reaction proceeds selectively at the phosphine centre of the dialkoxydialkyldiphosphine. The interaction of dialkoxydialkyldiphosphines with $PhPCl_2$ is unusual: as in the interaction of tetra-alkoxydiphosphines with PCl_3, the **P–P** bond undergoes oxidation-reduction cleavage and $PhPCl_2$ is reduced to $(PhP)_4$:

$$R_2P{-}P(OR)_2 + PhPCl_2 \rightarrow R_2PCl + (RO)_2PCl + (PhP)_4\ .$$

The interaction of silylated organic diphosphines with carboxylic acid chlorides leads to α-ketophosphonites containing **P–P** bonds[242]:



Alkyl halides, which are typical electrophiles, react with organic di- and poly-phosphines to form 1 : 1 phosphonium salts, which are entirely stable in the case of cyclopolyphosphines. With enhancement of the electron-donating properties of the substituents at the phosphorus atom, the rate of alkylation increases[243]. The monophosphonium salts derived from tetra-alkyldiphosphines and linear organic triphosphines are as a rule unstable, particularly for compounds with bulky substituents or in the case of 2,2-dialkoxy-1,1-dialkyldiphosphines[134,202]. Pentafluorophenylphosphine does not react with methyl iodide[243]. Cyclic monophosphonium salts may be obtained by the reaction of the readily available Ph_4P_2 with α,ω-dihalogenoalkylenes[244]:



$n = 2,\ X = ClO_4;\quad n = 3,\ 4,\ X = Br.$

The anomalous interaction of tetra-alkoxydiphosphines with methyl iodide[241] involves not only standard transformations via the mechanism of the Arbuzov rearrangement but also a rearrangement of the **P(O)–P** fragment to **P–O–P**:

$$(RO)_2P{-}P(OR)_2 + MeI \xrightarrow{-RI} [ROP(O)(Me){-}P(OR)_2] \rightarrow$$
$$\rightarrow [ROP(Me){-}O{-}P(OR)_2] \xrightarrow{MeI} Me_2P(O)OP(OR)_2\ .$$

Inorganic and organic diphosphines add to **C–C** bonds, which made it possible to draw a formal analogy between the reactivities of diphosphines and halogens[3]. In certain cases the mechanism of this addition is apparently quite unambiguous. Thus, under the conditions of a radical reaction (irradiation with ultraviolet light), F_4P_2 adds smoothly to olefins[245-247] and the ease of addition varies in the sequence ethylene > propene > but-2-ene, in agreement with the usual treatment within the framework of "steric hindrance". In this case one may speak of radical addition, since in the absence of irradiation the reaction does not occur at all at room temperature but does take place at 200°C, where F_4P_2 dissociates with formation of the PF_2 radical[247,248]. The reaction with perfluoro-olefins, which readily combine with nucleophilic intermediates, takes place slowly and with very low yields. Its stereochemistry may be inferred from the addition to cyclohexene, whereupon only the *trans*-isomer is formed[248], the ratio of compounds with axial and equatorial orientations of the PF_2 group being 6 : 4.

Tetramethyldiphosphine reacts slowly at 100°C with butadiene in the presence of azobisisobutyronitrile to form exclusively the 1,4-addition product[249]:

$$Me_2P{-}PMe_2 + CH_2{=}CH{-}CH{=}CH_2 \rightarrow Me_2P{-}CH_2{-}CH{=}CH{-}CH_2PMe_2\ .$$

In the dark the reaction does not occur even at 100°C.[250] The addition of tetra-alkyldiphosphines to a triple bond is also apparently a radical process, since it proceeds only under ultraviolet irradiation or in the presence of initiators and leads to a mixture of the *cis*- and *trans*-isomers[251]:

$$PhC{\equiv}CH + R_2P{-}PR_2 \rightarrow R_2PC(Ph){=}CHPR_2\ .$$

The tridentate ligand **(XXV)** is formed on ultraviolet irradiation at the wavelength at which F_4P_2 decomposes into F_2P radicals[252-254]:

$$F_2P{-}PF_2 + F_2PCH_2{-}CH{=}CH_2 \xrightarrow{h\nu} \underset{(XXV)}{F_2PCH_2{-}CH(PF_2){-}CH_2PF_2}\ .$$

Tetra-alkoxydiphosphines exhibit a high reactivity in reactions involving addition to multiple bonds activated in relation to nucleophilic attack[255]:

$$(RO)_2P{-}P(OR)_2 + CH_2{=}CH{-}R' \xrightarrow{20^\circ} (RO)_2PCH_2{-}CH(R')P(OR)_2\ .$$

When the electrophilicity of the double bond is reduced (methyl methacrylate), the rate of reaction falls and the completion of the reaction requires heating to 60°C. Tetra-alkoxydiphosphines do not add to butadiene even at 150°C.[130]

The optimum conditions for the homolytic dissociation of the P–P bond are known to involve irradiation (λ > 300 nm) or heating above 180°C.[256,257] The addition of tetraphenyldiphosphine to the C=O bonds of aldehydes occurs in the temperature range between 180° and 200°C, apparently via a free radical mechanism; the resulting ketophosphinites undergo a series of further transformations under the severe conditions employed[256].

It was mentioned above that the intermediate RP: (phosphinidene) is apparently a carbenoid species and cyclopolyphosphines can therefore be regarded as potential sources of phosphinidene, for example, for the synthesis of di-isopropenyl phenylphosphonites[258]:

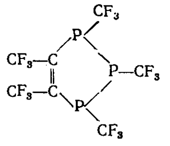
$$(PhP)_4 + 4Hg\,(CH_2COC_2H_5)_2 \rightarrow 4PhP\,[OC\,(Et){=}CH_2]_2 + 4Hg$$

or for the insertion in a non-metal–non-metal bond. The first steps in this field were made in the study of the reactions of phosphinidenes with disulphides[258] and α-diketones[259]:

$$(PhP)_5 \xrightarrow{160^\circ} 5\,[PhP{:}] \xrightarrow{Et{-}S{-}SEt} PhP\,(SEt)_2\ .$$

The formation of the intermediate PhP: in the course of addition to substituted butadienes was demonstrated mass-spectrometrically. The insertion of phosphinidene in the P–N, As–As, Si–Si, and N–N bonds was investigated subsequently[260]. The reaction of *N,N*-(dimethyl)dimethylphosphinous amide with $(CF_3P)_4$ resulted in the formation of a mixture, the main component of which was a phosphinidene complex, which was subsequently converted into the product of the insertion of phosphinidene in the P–N bond. The insertion in the As–As bond in tetramethyldiarsine took place in the same way. The interactions with tetramethylhydrazine and hexamethyldisilane could not be observed.

Mass-spectrometric data on tetra-alkyldiphosphines have been interpreted to demonstrate complete binding in these compounds[261–263], which, as stated above, is fairly controversial. In connection with the problem of the *p–d* conjugation, an attempt was made to generate radical-anions from the heterocycles (VIII), (IX), (XXII), and (XXVII):



$(MeP)_5$

(XXVI) (XXVII)

by treatment with the NaK alloy or electrochemically at −125° C.[265] It was found that (XXVII) and (VIII) do not yield radicals at all. The spin densities of the radical-anions (XI) and (XXVI) are localised at the C=C bonds and not at the phosphorus atom. This shows that the *d* orbitals do not stabilise the lowest-lying molecular orbital of the phosphorus atom, so that, among the elements of the Second Period, ready reduction to radical-anions is characteristic only of silicon in cyclopolysilanes.

Infrared and Raman spectroscopy has been used widely, particularly for the conformational analysis of diphosphines; on the other hand, for the detection of the P–P bond in compounds of a wide variety of types, ^{31}P NMR, and to a much lesser extent ^1H NMR, is the most informative method. The theoretical predictions of the chemical shifts in ^{31}P NMR spectra are still unsatisfactory, but the experimental data accumulated in this field for a wide variety of types of compounds with P–P bonds are now so extensive that identification based on analogies is entirely satisfactory. The constants for the spin–spin coupling between directly linked phosphorus atoms ($^1J_{P-P}$) lie within very broad limits (up to 1000 Hz), depending on the nature of the substituent at the phosphorus atom[265,266]; for two three-coordinated phosphorus atoms, $^1J_{P-P}$ varies in the range 100–400 Hz. The sign of the constant $^1J_{P-P}$ for organic diphosphines is known reliably in isolated instances[55] and is negative, while that of the constant $^1J_{P-N}$ is positive[267].

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Thus the chemistry of organic di- and poly-phosphines has been developing vigorously in recent years both as regards theory (stereochemistry and conformational analysis of OPC, discovery and identification of non-prototropic tautomerism, etc.) and practical applications (tetra-alkyldiphosphines initiate the copolymerisation of chloral with isocyanates[268] and are effective phosphorylating agents in sugar chemistry[269]). There is no doubt that this comparatively inadequately investigated field of the chemistry of OPC will attract increasing attention in the coming years.

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The Polarity and Structure of Unsaturated Derivatives of Four-coordinated Phosphorus

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The results of studies on the steric and electronic structures of unsaturated organophosphorus compounds with a four-coordinated phosphorus atom by the dipole moment method are surveyed. The polarity of the C–P bonds is analysed and the problems of conjugation and unsaturation in organophosphorus compounds are discussed. The orientation of the double bond and the conformation of the aryl groups attached to the phosphorus atom are examined. Data are presented on the conformational analysis of unsaturated organophosphorus compounds.
The bibliography includes 108 references.

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I. INTRODUCTION

Studies on steric structures with the aid of molecular dipole moment (DM) data are carried out by comparing the experimental moments with values calculated by means of an additive vector scheme[1]. The validity of the additive scheme may be regarded as firmly established; deviations from additivity indicate the occurrence of intramolecular interactions in the molecule. The determination of the absolute values and directions of bond moments is an extremely difficult problem and the reliability of the results depends in many respects on its solution. An additive computational scheme for phosphorus compounds is presented in Arshinova's review[2], who also examines the contribution of the dipole moment of the lone electron pair (LEP) of the phosphorus atom to the overall polarity of the molecule and shows that, in order to calculate the magnitude and direction of the molecular moment, even for asymmetrically substituted organophosphorus compounds (OPC), there is no need to introduce the vector of the LEP moment as an independent vector for purely mathematical reasons. For symmetrically substituted molecules, the LEP dipole moment is included implicitly in phosphorus bond moments. Any additive scheme for organic molecules is based primarily on the C–H bond moment using different DM values[1]. In the calculation of the OPC dipole moments one usually employs $m(\mathrm{H} \rightarrow \mathrm{C_{sp^3}}) = 0.28$ D, $m(\mathrm{H} \rightarrow \mathrm{C_{sp^2}}) = 0.70$ D, and $m(\mathrm{H} \rightarrow \mathrm{C_{sp}}) = 1.10$ D, determined from the line intensities in the infrared spectra[3], which makes it possible to compare the results of calculations by different investigators.

A number of reviews are devoted to the consideration of the steric structures of different OPC.[4-6] Studies on the steric and electronic structures of OPC by the method based on the Kerr effect are considered by Arshinova[2]. This review surveys and gives a systematic account of data on the polarity and structure of unsaturated OPC with a four-coordinated phosphorus atom obtained by the dipole moment method. Compounds with $\mathrm{P{-}C_{sp^2}}$ (where $\mathrm{C_{sp^2}}$ is a carbon atom in olefinic, carbonyl, and aromatic groups) and $\mathrm{P{-}C_{sp}}$ bonds are examined; whenever necessary, data obtained by other methods are invoked (infrared, Raman, ultraviolet, and NMR spectroscopy, the Kerr effect method, and electron diffraction).

II. THE POLARITY OF THE CARBON–PHOSPHORUS BOND

The considerable advances achieved in the study of the steric and electronic structures of organic molecules by electro-optical methods have been reflected also in studies on unsaturated OPC. Table 1 presents the results of investigations of phosphorus compounds with $\mathrm{P{-}C_{sp^2}}$ and $\mathrm{P{-}C_{sp}}$ bonds by the dipole moment method published up to 1978 (the numbering of the compounds in Table 1 will be used henceforth in this review). Table 2 presents the available literature data for the polarities of C–P bonds obtained for different types of OPC. It shows that the C–P bond moments are not constant; furthermore, they sometimes differ not only in absolute magnitude but also as regards direction. The majority of investigators have hitherto assumed that the $\mathrm{C_{sp^3}{-}P}$ bond moment is directed from the carbon to the phosphorus atom and that its absolute magnitude is ~0.6–0.8 D depending on the environment of the phosphorus atom. The $\mathrm{C_{sp^2}{-}P}$ bond moment is also directed to the phosphorus atom and, in conformity with the higher electronegativity of the sp^2-hybridised carbon atom, its absolute magnitude is somewhat smaller. Its direction (from C to P) has likewise been unambiguously established by comparing the dipole moments of triphenylphosphine and its *p*-substituted derivatives[12]. The sign of the $\mathrm{C_{sp}{-}P}$ bond moment is reversed, which is typical for all acetylenic compounds, including halogenoacetylenes [$m(\mathrm{Cl} \rightarrow \mathrm{C_{sp}}) = 0.66$ D].[40] The $\mathrm{P{-}C_{sp^3}}$ and $\mathrm{P{-}C_{sp^2}}$ bond moments with identical magnitudes and directions (from P to C) quoted by Mingaleva et al.[48] conflict with all other literature data. The discrepancy is probably due to the incorrect employment in the calculations of Mingaleva et al.[48] of the initial parameters: $m(\mathrm{P} \rightarrow \mathrm{O})$ was assumed to be 1.2 D, although there exist rigorous data showing that it is smaller and that it has the opposite direction[51]. Despite the fact that similar values have been obtained by Ishmaeva et al.[40] and Mingaleva et al.[48], the agreement must be regarded as fortuitous, since the two teams of investigators used different initial parameters.

Thus the following sequence has been observed for the C–P bond moments: $m(\mathrm{C_{sp^3}} \rightarrow \mathrm{P}) > m(\mathrm{C_{sp^2}} \rightarrow \mathrm{P}) > m(\mathrm{C_{sp}} \leftarrow \mathrm{P})$; the reversal of the sign of the $\mathrm{C_{sp}{-}P}$ bond moment in this series must be regarded as legitimate. The C–P bond moments calculated taking into account the dipole moments of the LEP of the phosphorus atom naturally differ from those where no account has been taken of the LEP. In this case a different sequence of C–P bond moments is observed[49]: $m(P \rightarrow C_{sp}) > m(P \rightarrow C_{sp^2}) > m(P \rightarrow C_{sp^3})$. In the calculation of the dipole moments of unsaturated OPC using the C–P bond moments with allowance for the LEP of the phosphorus atom, a new set of moments must be employed for all the remaining phosphorus bonds, also found taking into account the LEP. Since the absolute dipole moment of the phosphorus atom LEP is not known reliably (in any case it depends on the environment of the phosphorus atom) and the available literature data are contradictory, the present author suggests, in conformity with the evidence presented by Arshinova[2], that in the calculation of dipole moments of unsaturated OPC it is more useful to employ the moments of the C–P bonds and all other bonds without taking into account the LEP of the phosphorus atom.

Table 1. The experimental dipole moments of compounds of four-coordinated phosphorus containing an unsaturated carbon atom.

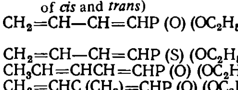
No. of cpd.	Compound	Solvent*	μ, D	References
	Compounds with a P^V–$C_{sp}2$ (olefin) bond			
(I)	$CH_2=CHP(O)(OC_2H_5)_2$	b	2.95	7,8,
		b	2.91	9
(II)	$CH_2=CHP(S)(OC_2H_5)_2$	c	2.76	10
(III)	$CH_2=CHP(O)(C_2H_5)_2$	c	4.55	11
(IV)	$CH_2=CHP(S)(C_2H_5)_2$	c	4.08	10
(V)	$CH_2=CHP(O)(C_6H_5)_2$	b	4.34	11
(VI)	$CH_2=CHP(O)(C_2H_5)(C_6H_5)$	b	4.31	11
(VII)	$CH_2=CHP(O)Cl_2$	c	3.52	10
		d	3.56	10
(VIII)	$CH_2=CHP(S)Cl_2$	d	3.11	10
(IX)	$CH_2=C(CH)_3P(O)(OC_2H_5)_2$	c	2.90	11
(X)	$CH_2=C(CN)P(O)(OC_2H_5)_2$	c	3.51	11
(XI)	$CH_2=C(Br)P(O)(OC_2H_5)_2$	c	2.59	11
(XII)	$CH_3CH=CHP(O)(OC_2H_5)_2$	b	2.92	9,12
(XIII)	$C_2H_5CH=CHP(O)(OC_2H_5)_2$ (*cis*)	b	2.89	9
(XIV)	$C_2H_5CH=CHP(O)(OC_2H_5)_2$ (10% (*cis*), 90% *trans*)	b	3.03	9
(XV)	iso-$C_3H_7CH=CHP(O)(OC_2H_5)_2$ (90% (*cis*), 10% *trans*)	b	2.90	9
(XVI)	$NCCH=CHP(O)(OC_2H_5)_2$ *trans*)	c	3.99—4.02	**
(XVII)	n-$C_4H_9OCH=CHP(O)(OC_2H_5)_2$ (*trans*)	b	3.38	11
(XVIII)	n-$C_4H_9SCH=CHP(O)(OC_2H_5)_2$ (*trans*)	b	3.42	**
(XIX)		b	4.10	**
(XX)	$C_2H_5OCH=CHP(O)(OC_6H_5)_2$	b	4.04	**
(XXI)	n-$C_4H_9OCH=CHP(O)(C_6H_5)_2$ (*trans*)	b	4.36	13
(XXII)	n-$C_4H_9OCH=CHP(O)Cl_2$	c	4.46	11
(XXIII)	$(C_2H_5O)_2P(O)CH=CHP(O)(OC_2H_5)_2$	c	3.52	**
(XXIV)	$CH_3CH=C(CH_3)P(O)(OC_2H_5)_2$	b	2.85	9
(XXV)	$Cl(CH_3)C=CHP(O)(OC_2H_5)_2$ (*cis*)		3.35	14,15
(XXVI)	$Cl(CH_3)C=CHP(O)(OC_2H_5)_2$ (*trans*)	—	2.92	15
(XXVII)	$Cl(t\text{-}C_4H_9)C=CHP(O)(OC_2H_5)_2$ (*cis*)	—	3.51	15
(XXVIII)	$Cl(t\text{-}C_4H_9)C=CHP(O)(OC_2H_5)_2$ (*trans*)	—	2.92	15
(XXIX)	$Cl(C_6H_5)C=CHP(O)(OC_2H_5)_2$	—	3.68	14
(XXX)	$ClCH=C(CH_3)P(O)(OC_2H_5)_2$ (*trans*)	—	3.11	15
(XXXI)	$Cl(OC_2H_5)C=CHP(O)(OC_2H_5)_2$ (mixture of *cis* and *trans*)	—	3.54	15
(XXXII)	$CH_2=CH—CH=CHP(O)(OC_2H_5)_2$ (*trans*)	b	3.04	7,8
			2.92	9
(XXXIII)	$CH_2=CH—CH=CHP(S)(OC_2H_5)_2$ (*trans*)	b	2.91	7
(XXXIV)	$CH_3CH=CHCH=CHP(O)(OC_2H_5)_2$ (*trans*)	b	3.07	9
(XXXV)	$CH_2=CHC(CH_3)=CHP(O)(OC_2H_5)_2$ (*cis*: *trans* = 1 : 1)	b	2.94	9
(XXXVI)	$CH_2=CHC(Cl)=CHP(O)(OC_2H_5)_2$	—	2.84	14
(XXXVII)	$C_6H_5CH=CHP(O)(OC_2H_5)_2$	b	3.68	12,16
		b	3.13	17
		c	3.18	17
(XXXVIII)	$C_6H_5CH=CHP(O)Cl_2$	c	4.30	17
(XXXIX)	$C_6H_5CH=CHP(S)(CH_3)_2$	b	4.79	12,18
(XL)	$C_6H_5CH=CHP(S)(C_6H_5)_2$	b	4.80	12,18
(XLI)	$(C_6H_5CH=CH)_3PS$	b	4.80	12,18
(XLII)	$C_6H_5CH=C(CN)P(O)(OC_2H_5)_2$	c	2.58	8
(XLIII)	p-$ClC_6H_4CH=CHP(O)(OC_2H_5)_2$	c	2.87	17
(XLIV)	p-$ClC_6H_4CH=CHP(O)Cl_2$	c	3.14	17
(XLV)	p-$ClC_6H_4CH=C(CN)P(O)(OC_2H_5)_2$	c	2.67	8,17
(XLVI)	p-$BrC_6H_4CH=C(CN)P(O)(OC_2H_5)_2$	c	2.62	8,17
(XLVII)	p-$NO_2C_6H_4CH=C(CN)P(O)(OC_2H_5)_2$	b	4.78	8,17

Table 1 (contd.).

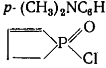
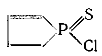
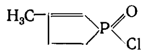
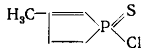
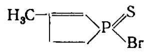
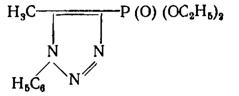
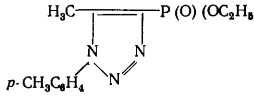
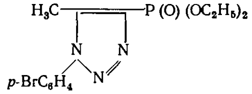
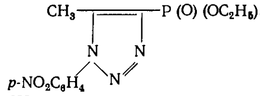
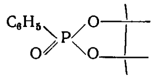
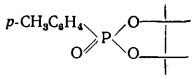
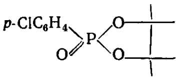
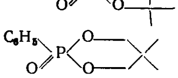
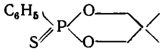
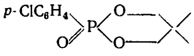
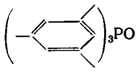
No. of cpd.	Compound	Solvent*	μ, D	References
(XLVIII)	m-$NO_2C_6H_4CH=C(CN)P(O)(OC_2H_5)_2$	b	4.14	8.17
(XLIX)	p-$CH_3OC_6H_4CH=C(CN)P(O)(OC_2H_5)_2$	c	3.30	8.17
(L)	p-$(CH_3)_2NC_6H_4CH=C(CN)P(O)(OC_2H_5)_2$	b	4.08	8.17
(LI)		—	4.69	19
(LII)		—	3.56	19
(LIII)		—	5.37	19
(LIV)		—	4.95	19
(LV)		—	4.58	19
(LVI)		b	4.76	20
(LVII)		b	4.33	20
(LVIII)		b	2.27	20
(LIX)		b	2.42	20
(LX)	$CH_2=C=CHP(O)(OC_2H_5)_2$	b	3.14	9
(LXI)	$CH_3CH=C=CHP(O)(OC_2H_5)_2$	b	3.32	9
(LXII)	$(CH_3)_2C=C=CHP(O)(OCH_3)_2$	b	3.46	9
(LXIII)	$(CH_3)_2C=C=CHP(O)(OC_2H_5)_2$	b	3.38	9
(LXIV)	$CH_2=C=C(CH_3)P(O)(OCH_3)_2$	b	3.14	9
(LXV)	$CH_2=C=C(CH_3)P(O)(OC_2H_5)_2$	b	3.07	9
	Compounds with a P^V–$C_{sp}2$ (carbonyl) bond			
(LXVI)	$CH_3C(O)P(O)(OC_2H_5)_2$	c	3.10	21
(LXVII)	$C_6H_5C(O)P(O)(OCH_3)_2$	c	2.93	12
(LXVIII)	$C_6H_5C(O)P(O)(OC_2H_5)_2$	c	2.76	21
(LXIX)	$C_6H_5C(O)P(O)(C_2H_5)(OC_2H_5)$	c	2.44	21
(LXX)	$C_6H_5C(O)P(O)(C_6H_5)(OC_2H_5)$	c	2.72	21
(LXXI)	$C_6H_5C(O)P(O)(C_2H_5)_2$	c	2.28	21
(LXXII)	$C_6H_5C(O)P(O)(C_6H_5)_2$	b	2.69	21
(LXXIII)	p-$CH_3C_6H_4C(O)P(O)(OC_2H_5)_2$	c	2.88	21
(LXXIV)	p-$CH_3OC_6H_4C(O)P(O)(OC_2H_5)_2$	c	3,35	21
(LXXV)	p-$FC_6H_4C(O)P(O)(OC_2H_5)_2$	c	2,73	**
(LXXVI)	p-$ClC_6H_4C(O)P(O)(OC_2H_5)_2$	c	2.79	21
(LXXVII)	o-$ClC_6H_4C(O)P(O)(OC_2H_5)_2$	c	3.11	21
(LXXVIII)	(m-$ClC_6H_4C(O)P(O)(OC_2H_5)_2$	c	2.77	21
(LXXIX)	(p-$BrC_6H_4C(O)P(O)(OC_2H_5)_2$	c	2.80	21
(LXXX)	(m-$BrC_6H_4C(O)P(O)(OC_2H_5)_2$	c	2.88	21
(LXXXI)	(p-$NO_2C_6H_4C(O)P(O)(OC_2H_5)_2$	b	4.84	21
(LXXXII)	$(C_2H_5)_2NC(O)P(O)(OC_2H_5)_2$	b	2.91	12,22
		—	2.93	12
(LXXXIII)	$(C_2H_5)_2NC(O)P(O)(OC_3H_7)_2$	b	3.02	12,22
(LXXXIV)	$(C_2H_5)_2NC(O)P(O)(OC_3H_7\text{-iso})_2$	b	2.88	12,22
(LXXXV)	$(C_2H_5)_2NC(O)P(O)(OC_4H_9)_2$	b	3.09	12,22
(LXXXVI)	$(C_2H_5)_2NC(O)P(O)(OC_5H_{11}\text{-iso})_2$	b	2.92	12,22
(LXXXVII)	$(C_2H_5)_2NC(O)P(O)(OC_6H_{13})_2$	b	2.94	12,22
	Compounds with a P^V–$C_{sp}2$ (aryl) bond			
(LXXXVIII)	$C_6H_5P(O)(OCH_3)_2$	c	2.95	23
(LXXXIX)	$C_6H_5P(O)(OC_2H_5)_2$	c	3.04	24
(XC)	$C_6H_5P(O)Cl_2$	c	3.99	24
(XCI)	p-$CH_3C_6H_4P(O)(OCH_3)_2$	c	3.37	23
(XCII)	p-$CH_3C_6H_4P(O)(OC_2H_5)_2$	c	3.23	24
(XCIII)	p-$CH_3OC_6H_4P(O)(OCH_3)_2$	c	3.39	23
(XCIV)	p-$CH_3OC_6H_4P(O)(OC_2H_5)_2$	c	3.31	24
(XCV)	p-$ClC_6H_4P(O)(OCH_3)_2$	c	2.63	23
(XCVI)	p-$ClC_6H_4P(O)(OC_2H_5)_2$	c	2.83	24
(XCVII)	p-$BrC_6H_4P(O)(OC_2H_5)_2$	c	2.81	24
(XCVIII)	p-$NO_2C_6H_4P(S)(OC_2H_5)_2$	b	4.98	12
(XCIX)		c	5.18	25
(C)		c	5.13	25

Table 1 (contd.).

No. of cpd.	Compound	Solvent*	μ, D	References
(CI)		c	5.32	25
(CII)		b	4.59; 5.73	25,26
		c	4.36; 4.51	25,27
		d	4.96	27
(CIII)		d	4.21	27
(CIV)		c	4.46	25
(CV)		d	3.82	27
(CVI)		d	3,28	27
(CVII)	$C_6H_5(CH_3)P(O)OCH_3$	b	3.79—3,82	28
		c	3.80	29
(CVIII)	$C_6H_5(CH_3)P(O)OC_6H_5$	c	3.88	29
(CIX)	$C_6H_5(CH_3)P(O)OC_6H_4NO_2$-*n*	c	6.25	29
(CX)	*p*-$ClC_6H_4(CH_3)P(O)OCH_3$	b	3.06—3.10	28
(CXI)	*p*-$CH_3C_6H_4P(O)(CH_3)_2$	c	4,30	30
(CXII)	*p*-$CH_3C_6H_4P(O)(C_4H_9$-t)2	c	4.85	30
(CXIII)	*p*-$CNC_6H_4P(O)(CH_3)_2$	d	4.60	30
(CXIV)	$(C_6H_5)_2P(O)OC_2H_5$	b	3.65—3.70	28
(CXV)	$(C_6H_5)_2P(S)SCH_3$	b	4.01—4.06	31
(CXVI)	$(C_6H_5)_2P(S)SSP(S)(C_6H_5)_2$	b	4.18—4.26	31
(CXVII)	(*p*-$ClC_6H_4)_2P(O)OC_2H_5$	b	3.12—3.18	28
(CXVIII)	(*p*-$ClC_6H_4)_2P(S)SCH_3$	b	2.89—2.96	31
(CXIX)	(*p*-$ClC_6H_4)_2P(S)SSP(S)(C_6H_4Cl$-*n*$)_2$	b	2.28—2.46	31
(CXX)	(*p*-$ClC_6H_4)_2P(S)SH$	b	2.62—2.70	31
(CXXI)	$(C_6H_5)_2P(O)CH_2CN$	b	3.76	32
(CXXII)	$(C_6H_5)_2P(O)CCl_3$	c	3.81	33
(CXXIII)	(*p*-$CH_3C_6H_4)_2P(O)CCl_3$	c	4.75	33
(CXXIV)	(*p*-$ClC_6H_4)_2P(O)CCl_3$	c	2.82	33
	Symmetrical triarylphosphine oxides			
(CXXV)	$(C_6H_5)_3PO$	*p*-x	4.403	12
		b	4.49; 4.44; 4.42; 4.53	12,34, 35,36,37
		d	4.55	12
(CXXVI)	$(C_6H_5)_3PS$	b	4.89; 4.79; 4.83	12,37,38
(CXXVII)	(*p*-$ClC_6H_4)_3PO$	c	3.14	35
		b	2.95; 3.01	12,37
(CXXVIII)	(*p*-$ClC_6H_4)_3PS$	b	3.14	37
(CXXIX)	(*m*-$ClC_6H_4)_3PO$	b	4.41	37
		c	4.78	35
(CXXX)	(*m*-$ClC_6H_4)_3PS$	b	4.60	37
(CXXXI)	(*p*-$FC_6H_4)_3PO$	b	2.98	37
(CXXXII)	(*p*-$FC_6H_4)_3PS$	b	3.23	37
(CXXXIII)	(*m*-$FC_6H_4)_3PO$	b	4.30	37
(CXXXIV)	(*m*-$FC_6H_4)_3PS$	b	4.51	37
(CXXXV)	(*p*-$CH_3C_6H_4)_3PO$	c	5.02	35
		b	4.88	36
(CXXXVI)	(*m*-$CH_3C_6H_4)_3PO$	c	4.57	35
(CXXXVII)		b	4.18	36
	Asymmetric triarylphosphine oxides			
(CXXXVIII)	$(C_6H_5)_2P(O)C_6H_4OCH_3$-*p*	d	4.83	12
(CXXXIX)	$(C_6H_5)_2P(S)C_6H_4OCH_3$-*p*	d	5.19	12
(CXL)	$(C_6H_5)_2P(O)C_6H_4Cl$-*p*	d	4.37	12
(CXLI)	$(C_6H_5)_2P(S)C_6H_4Cl$-*p*	d	4.81	12
(CXLII)	$(C_6H_5)_2P(O)C_6H_4Br$-*p*	d	4.57	12
(CXLIII)	$(C_6H_5)_2P(S)C_6H_4Br$-*p*	d	4.71	12
(CXLIV)	$(C_6H_5)_2P(O)C_6H_4N(CH_3)_2$-*p*	d	5.71	12
(CXLV)	$(C_6H_5)_2P(S)C_6H_4N(CH_3)_2$-*p*	d	6.42	12
	Compounds with a P^V–C_{sp} bond			
(CXLVI)	$HC\equiv CP(O)(OC_2H_5)_2$	b	3.64; 3.86	39,40
(CXLVII)	$CH_3C\equiv CP(O)(OC_2H_5)_2$	c	3.69	40
		b	3.78; 3.94	12,39,40
(CXLVIII)	$CH_3C\equiv CP(O)(OC_4H_9)_2$	b	3.93	12,41
(CXLIX)	$CH_3C\equiv CP(S)(CH_3)_2$	b	4.90	42
(CL)	$CH_3C\equiv CP(O)(C_2H_5)_2$	c	4.59	40
(CLI)	$CH_3C\equiv CP(O)(C_6H_5)_2$	c	4.48	40
(CLII)	$CH_3C\equiv CP(O)Cl_2$	c	3.92	40
(CLIII)	$ClC\equiv CP(O)(OC_2H_5)_2$	b	3.44; 3.54	39,40
(CLIV)	$BrC\equiv CP(O)(OC_2H_5)_2$	b	3.66	39
(CLV)	$(C_2H_5)_2NC\equiv CP(O)(OC_2H_5)_2$	—	5.06	43
		b	3.71	**
(CLVI)	$CH_2=CHC\equiv CP(O)(OC_2H_5)_2$	b	3.88	44
(CLVII)	$CH_2=CHC\equiv CP(S)(CH_3)_2$	b	4.73	42
(CLVIII)	$CH_2=C(CH_3)C\equiv CP(O)(OC_2H_5)_2$	b	3.84	44
(CLIX)	$CH_3CH=CHC\equiv CP(O)(OC_2H_5)_2$	b	4.06	12,44
(CLX)	$C_2H_5C\equiv CC\equiv CP(O)(OC_2H_5)_2$	b	4.39	16
(CLXI)	$C_6H_5C\equiv CP(O)(OC_2H_5)_2$	b	4.17	12,16
(CLXII)	$C_6H_5C\equiv CP(S)(CH_3)_2$	b	4.91	12,42
(CLXIII)	$(CH_3C\equiv C)_2P(O)CH_3$	b	4.98	12,42
(CLXIV)	$(C_6H_5C\equiv C)_2P(O)CH_3$	b	5.18	12,42
(CLXV)	$(C_6H_5C\equiv C)_2P(S)CH_3$	b	5.14	12,42
(CLXVI)	$(C_6H_5C\equiv C)_2P(S)C_6H_5$	b	5.20	12,42
(CLXVII)	$(C_6H_5C\equiv C)_2P(S)CH=CHC_6H_5$	b	5.12	12,42
(CLXVIII)	$(CH_3C\equiv C)_3PS$	b	5.20	42
(CLXIX)	$(C_6H_5C\equiv C)_3PS$	b	5.32	42
(CLXX)	(*p*-$CH_3C_6H_4C\equiv C)_3PS$	b	5.47	42
(CLXXI)	[*o*, *p*-$(CH_3)_2C_6H_3C\equiv C]_3PS$	b	5.78	42

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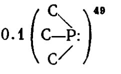
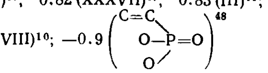
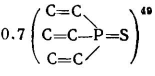
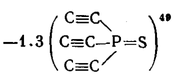
*Solvent: b = benzene; c = carbon tetrachlorides; d = dioxan; *p*-x = *p*-xylene.

**Data of the author of the review.

Table 2. The dipole moments (in D) $m(C_{sp^3}-P)$, $m(C_{sp^2}-P)$, and $m(C_{sp}-P)$.

Bond	Without allowance for the P atom LEP dipole moment	With allowance for P atom LEP dipole moment
C_{sp^3} — P	0.55 (Me_3P)[45—46]; 0.81 (Et_3P)[8]; 0.94 (Et_2POEt)[50]; 1.11* (Et_3P)[47]; —0.7 (av.)[48]	—0.1  [49]
C_{sp^2} (olefin)-P	0.30 (V)[11]; 0.37 (VI)[11]; 0.40 (VII)[10]; 0.56 (I)[8]; 0.60 (IV)[10]; 0.82 (XXXVII)[17]; 0.83 (III)[11]; —0.09 (VIII)[10]; —0.9  [48]	—0.7  [49]
C_{sp^2} (phenyl)-P	0.38—0.39 (Ph_3P)[21,37,47]; 0.69 (XC)[24]; 0.70 (LXXXIX)[24]; 0.7** (Ph_3P)[50]; 1.40*** from data in Ref.31	—0.4 (Ph_3P)[49]
C_{sp} — P	—0.20 (CL)[40]; —0.30 (CLII)[40]; —0.30 (av.)[40]; —0.43 (CLI)[40]; ~—0.7 (av.)[48]	—1.3  [49]

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*The authors[17] evidently have in mind the group moment of the Et–P bond, so that $m(C_{sp^3}-P) = 1.11-0.28 = 0.83$ D.

**Here it is assumed that $m(H-C_{sp^2}) = 0.31$ D.

***Here $m(H-C_{sp^2}) = 0$; in all other instances the authors employed the values of m(H– C) quoted by Gribov and Popov[3].

The C_{sp^2}– P bond moments are subject to the particularly strong influence of the substituents both at the phosphorus atom and in the unsaturated group (there are very few data for C_{sp}–P bonds). An additional illustration of the foregoing considerations is provided by the experimental dipole moments of the following compounds: 2.91–2.95 D [7-9] for (I), 2.92–3.04 D [7-9] for (XXXII), and 3.13–3.18 D [17] and 3.68 D [16] for (XXXVII). With increase of the length of the π-electron system at the phosphorus atom, the experimental dipole moment increases, although calculation based on the additive scheme yields the same value for different compounds. The conjugation in buta-1,3-dienylphosphonates, buta-1,3-dienylphosphonothioates[8,52], and styrylphosphonates[53,54] (in which the C=C and P=O groups are in the *trans*-positions) has been detected by infrared and Raman spectroscopic methods. Consequently a theoretical calculation of the dipole moments of unsaturated OPC using the same value of $m(C_{sp^2}-P)$ is possible only for compounds with analogous structures. m(R–P) (where R is an unsaturated group), which is equal to the sum of the R′–C_{sp^2} and C_{sp^2}–P bond moments, the conjugation moment of the π-electron system incorporating the phosphorus atom, and the interaction moment arising when substituents (R′ = H, CH_3, etc.) are introduced into the π-electron system, may be calculated with the aid of data for model compounds for each series of unsaturated OPC:

$$m\,(\mathrm{R—P}) = m\,(\mathrm{R'—C}_{sp^2}) + m\,(\mathrm{C}_{sp^2} — \mathrm{P}) + m_{\mathrm{conjug.}} + m_{\mathrm{interact.}}$$

The conjugation moment and the intrinsic moment of the C_{sp^2}–P bond cannot be calculated separately; the instances where it is possible to isolate the interaction moments will be discussed below. Thus the C_{sp^2}–P bond moments determined are not the true moments, representing effective quantities which include the conjugation moment and frequently also the interaction moment. However, these moments may be used to estimate the conjugation effects in series of analogous compounds when only one end of the conjugated system is altered.

An additional difficulty in the study of unsaturated phosphonates is the necessity to know the magnitude and direction of the dipole moment of the irregular $P(O)(OR)_2$ group. The latter had been calculated by Mingaleva et al.[48], but was subsequently re-evaluated, for reasons stated, by Ishmaeva et al.[8] (2.30 D was obtained). The vector of the effective dipole moment of this group forms an angle of 72° with the C–P bond, which corresponds to the *gauche*-orientation (with some distortion in the direction of *cis*-orientation) of the ethyl groups in relation to the P–O bond.

Table 3. The effective values of $m(C_{sp^2}–P)$ in phosphonates[8,17].

Compound	$m(\mathrm{C}_{sp^2}\rightarrow\mathrm{P})$, D
(I)	0.56
(XXXII)	0.70
(LXXXVIII)	0.69
(XXXVII)	0.82

The determination of the magnitude and direction of the effective dipole moment of the dialkylphosphono-group made it possible to estimate the effective C_{sp^2}–P bond moments in various unsaturated phosphonates (Table 3). The high P–C_{sp^2} bond moments, with the moment directed towards the carbon atom, which are obtained on solving a quadratic equation, can apparently be excluded from consideration, since these data do not agree with the electronegativities of the C and P atoms and also conflict with ideas concerning the polarity of single bonds involving phosphorus. Table 3 shows that the C–P bond moments in unsaturated phosphonates unsubstituted in the π-electron system vary relatively little (~0.6–0.8 D).

The C_{sp^2}–P bond orders in vinylphosphine oxides and sulphides vary within wide limits (Table 4). The effective C_{sp^2}–P bond orders in compounds (III)–(VI), listed in Table 4, can be satisfactorily accounted for by steric effects and are consistent with the ideas concerning the electronic influence of phosphorus-containing substituents[55]. The variation of the C_{sp^2}–P bond moment may serve as evidence for the variation of conjugation in the π-electron system. Accordingly, one may expect a higher value of $m(C_{sp^2}–P)$ for buta-1,3-dienylphosphonate (**XXXII**) than for vinylphosphonate (I) and a higher value for styrylphosphonate (**XXXVII**) than for phenylphosphonate (**LXXXIX**), which is in fact observed (Table 3). The determination of the effective values of $m(C_{sp^2}–P)$ made it possible to estimate the moments of the interaction of the vinyl and phenyl groups with the diethylphosphono-group in esters of buta-1,3-dienyl- and styryl-phosphonic acids, which are respectively 0.14 and 0.23 D.[17] Evidently there is some electron transfer in the π-electron system, which leads to the orientation of the overall moment of the hydrocarbon groups towards the phosphorus atom. The moment of the interaction with the sulphur-containing compound (XXXIII) also proved to be close to these values (0.20 D). The interaction moment obtained for compound (XLIII) (1.12 D) indicates an appreciable involvement of the phosphorus-containing group in the direct polar conjugation of the overall chain.

Table 4. The effective values of $m(C_{sp^2}–P)$ in vinylphosphine oxides and sulphides[10-11].

Cpd.	$m\,(\mathrm{C}_{sp^2}\rightarrow\mathrm{P})$, D	Cpd.	$m\,(\mathrm{C}_{sp^2}\rightarrow\mathrm{P})$, D
(III)	0.83	(V)	0.30
(IV)	0.60	(VII)	0.40
(VI)	0.37	(VIII)	—0.09

The interaction moments may be determined also for *p*-substituted phenylphosphonates (Table 5). The values calculated for them do not agree with experiment, which is due to the interaction of the *p*-substituents in the phenyl group with the $P(O)(OR)_2$ group. The interaction moments directed along the C_{sp^2}–P bond reach values ⩾ 1 D, which indicates an appreciable involvement of the phosphorus-containing fragment in the overall conjugation chain. An excellent correlation has been found (r = 0.999) between the experimental dipole moments of *p*-substituted phenylphosphonates and the Hammett σ constants, which indicates an interaction involving conjugation. The experimental dipole moments of *p*-substituted benzoylphosphonates[21] exceed the calculated values by 0.6–0.7 D. Although it is not possible to separate the influence of the C–O and P–O groups and to calculate the interaction moments, nevertheless, the significant influence of the phosphorus-containing group in this instance may be recognised. It follows from the fact that the interaction moment in *p*-methoxyacetophenone is only 0.24 D while in *p*-chloro- and *p*-bromo-acetophenones the experimental values are actually somewhat lower than those calculated assuming additivity. This conclusion is confirmed by the results obtained in infrared and ultraviolet spectroscopic studies on benzoylphosphonates[56-64].

Thus the π-electron system in the unsaturated OPC investigated interacts with the phosphorus-containing groups. The problem of the involvement in conjugation of the tetrahedral phosphorus atom has been frequently discussed in the literature[7,16,21,24,52-54,56,65-74]. It has been suggested that the conjugation is both of the π–π and $p\pi$–$d\pi$ type, but the mechanism of the interaction of unsaturated systems with phosphorus-containing groups still cannot be regarded as accurately established. The hypothesis of the $p\pi-d\pi$ interaction in these systems, widely used by chemists, has been questioned[75], because the *d* orbitals of the phosphorus atom are fairly diffuse and energetically unsuitable and their appreciable overlapping with the orbitals of the groups attached to phosphorus is unlikely, i.e. the quantitative aspect of the problem of the role of the $p\pi-d\pi$ interaction remains controversial[6]. There is nevertheless no doubt that electron delocalisation takes place in OPC molecules containing unsaturated groups with participation of the phosphorus atom or the entire phosphorus-containing group, which the present author attempted to demonstrate by the dipole moment method.

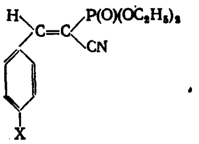
Table 5. The dipole moments of p-$XC_6H_4P(O)(OC_2H_5)_2$.[24]

Compound	X	μ_{exp}, D	μ_{calc}, D	m_{react}, D
(XCII)	CH_3	3,23	3.30	—0,10
(XCVI)	Cl	2,83	2,25	1.27
(XCVII)	Br	2,81	2,26	1,22
(XCIV)	CH_3O	3.31	3,21	0,98

III. THE STERIC ORIENTATION OF THE DOUBLE BOND AT THE PHOSPHORUS ATOM

Another important task in the study of unsaturated OPC is investigation of their steric structure. There are very few electron diffraction or X-ray diffraction literature data for these compounds (see reviews[4-6]) and they are mainly concerned with compounds containing a $P-C_{sp^2}$ bond (phenyl) (see, for example, Refs. 76–80). There have been several studies on compounds with a $P-C_{sp^2}$ (olefin) bond[81-83] and acyclic OPC with a $P-C_{sp^2}$ (olefin) bond have been investigated in only one study[82] in relation to vinylphosphonic dichloride and divinylphosphinic chloride. It has been shown[82] that the main conformation of both compounds is one with the *cis*- (or nearly *cis*-) disposition of the C=C and P=O bonds, which are virtually coplanar. There is also other evidence for the preferential disposition of the C=C and P=O bonds in a single plane[52,84,85].

The dipole moment method is important and fairly reliable for the determination of the configurations of unsaturated OPC. For example, it has been established by the dipole moment method, in agreement with NMR data[86], that the benzene ring and the diethylphosphonogroup in α-cyanostyrylphosphonates are in the *trans*-positions[17] (Table 6):



Furthermore, the dipole moment method makes it possible to investigate the conformational isomerism relative to the $P-C_{sp^2}$ and other bonds involving phosphorus (P–O, P–S, P–Se, etc.). Estimation of the polarity of the $P-C_{sp^2}$ bond in styrylphosphonic acid esters made it possible to assess the conformational isomerism of α-cyanostyrylphosphonates, i.e. to examine the rotation about the $P-C_{sp^2}$ (olefin) bond[17]. The presence of the cyano-group in these compounds is responsible for the different polarities of the *s*-*cis*- and *s*-*trans*-conformers:

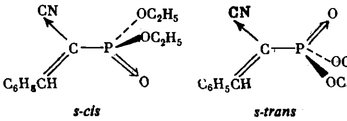


Table 6. The dipole moments of p-$XC_6H_4CH=C(CN)P.(O)(OC_2H_5)_2$.[17]

Compound	X	μ_{exp}, D	μ_{calc}, D	
			trans	*cis*
(XLV)	Cl	2.67	2,73	1,99
(XLVI)	Br	2.62	2.74	1.96
(XLVII)	NO_2	4.78	4.53	3.40

Comparison of the dipole moments calculated for the two conformers with the experimental dipole moment of diethyl-α-cyanostyrylphosphonate (XLII) indicates the preferential (approximately 80%) occurrence of the *s*-*cis*-form, i.e. the conformer with the antiparallel direction of the dipoles of the substituents (CN and P=O). The conformational isomerism in relation to the $P-C_{sp^2}$ bond in α- and β-substituted vinylphosphonates has been investigated[10,11]:

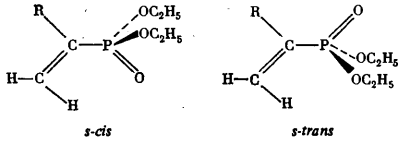


Table 7. The dipole moments of $CH_2=C(R)P(O)(OC_2H_5)_2$.[11]

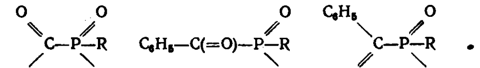
Compound	R	μ_{exp}, D	μ_{calc}, D		
			s-*trans*	*s*-*cis*	$n_{s\text{-}cis}$, %
(IX)	CH_3	2.90	2.86	3.30	10
(X)	CN	3.51	5.24	0.88	60
(XI)	Br	2,59	3.64	1.60	60

Table 7 presents the experimental and calculated dipole moments of α-substituted vinylphosphonates. The tabulated data show that the conformer with the antiparallel directions of the dipoles is more stable in all the compounds. The preferred *s*-*trans*-form of α-methylvinylphosphonic dichloride has also been detected by infrared spectroscopy[87]. The *s*-*cis*–*s*-*trans* isomerism of vinylphosphonates with an irregular substituent in the β-position and a non-uniform distribution of conformations can likewise be investigated, since the dipole moments of the two isomers are different. According to ^{1}H NMR data[13], the RO and P=O groups in β-alkoxyvinylphosphonates are in the *trans*-positions relative to the C=C bond. Comparison of the calculated and experimental dipole moments of these compounds (Table 8) shows that the conformer with the *s-trans*-disposition of the C=C and P=O bonds predominates in all the compounds[13].

Table 8. The dipole moments of $C_4H_9OCH{=}CHP(O)R_2$.[13]

Compound	R	μ_{exp}, D	μ_{calc}, D		n_s-trans, %
			s-trans	*s*-cis	
(XVII)	OC_2H_5	3.41	3.46	3.97	100
(XXII)	Cl	4.46	4.39	4.92	90
(XXI)	C_6H_5	4.36	4.18	4.70	70

The isomerism relative to the $P{-}C_{sp^2}$ (carbonyl) bond has been investigated for benzoylphosphine oxides as an example[21]. The latter are convenient subjects for the examination of rotation about the $P{-}C_{sp^2}$ bond in contrast to the unsubstituted vinyl- and buta-1,3-dienyl-phosphonates, where the polarities of the *s-cis*- and *s-trans*-conformers are independent of rotation about the bond. There is as yet no unanimous view in the literature concerning the relative positions of the C=O and P=O groups. A structure with the C=O and P=O groups in mutually perpendicular planes has been suggested[88]. According to other data[67], a planar disposition of the π-electron system and the P=O bond is the most favourable; in this case there is a possibility of two rotational isomers with the *s-cis*- and *s-trans*-dispositions of the C=O and P=O groups:



s-cis $C{=}O \perp P{=}O$ *s-trans*

Table 9 presents the experimental and calculated dipole moments of benzoyldiethylphosphine oxide (LXXI) and benzoyldiphenylphosphine oxide (LXXII).[21] If the C=O and P=O groups were located in mutually perpendicular planes, the experimental dipole moments of (LXXI) and (LXXII) would be close to 4.59 D, whereas in fact they are consistent with an equilibrium between *s-cis*- and *s-trans*-forms, where the content of the latter is approximately 90–95%. When the experimental and calculated dipole moments of benzoylphosphinates[21] are examined, the *s-trans*-conformation also proves to be preferred (approximately 90–95%), i.e. there is virtually no rotation about the $C_{sp^2}{-}P$ bond. It is noteworthy that the strong dipoles of the substituting groups in the preferred conformations (C≡N and P=O, C=O and P=O) are oriented antiparallel, which indicates a significant influence of electrostatic factors on the steric structure. There is a conformational equilibrium in benzoylphosphonates between the *s-cis*- and *s-trans*-forms, with the latter predominating slightly (~60%).[21]

The conclusion that the O=C–P=O system is not rigid has been questioned[89]. The authors[89] studied benzoylphosphonates by infrared spectroscopy and concluded that there is no rotation about the $P{-}C_{sp^2}$ bond, because the absorption band of the carbonyl group is not split. The *s-trans*-form (which predominates for benzoylphosphinates and benzoylphosphine oxides also according to dipole moment data) has been suggested as the only isomer of these compounds. If it is supposed that there is a non-planar *gauche*-disposition of the C=O and P=O groups in benzoylphosphonate (LXVIII), the dipole moment calculated for this form is found to be close to the experimental value. However, the occurrence of this form has been rejected[89].

Table 9. The dipole moments of benzoyldiethylphosphine oxide and benzoyldiphenylphosphine oxide[21].

Compound	μ_{exp}, D	μ_{calc}, D			n_s,*trans*, %
		s-cis	$C{=}O \perp P{=}O$	*s-trans*	
(LXXI)	2.28	6.25	4.59	1.73	95
(LXXII)	2.69	6.25	4.59	1.73	90

The available literature data concerning the mutual disposition of the C=O and P=O groups in benzoylphosphonates[21,88,89] are probably insufficient for a final conclusion. At any rate, the absence of the splitting of the ν(C=O) band is not adequate evidence for the rigidity of the O=C–P=O system, because the forms involved in equilibrium may have similar spectroscopic characteristics, and may be indistinguishable in the infrared spectra. Nor can one explain the difference between the calculated dipole moment (0.78 D)[21] of the *s-trans*-form of benzoylphosphonate (LXVIII) and the experimental value (3.10 D) by a deviation from additivity owing to the interactions of the carbonyl and phosphoryl groups (as was done by Laskorin et al.[89]). Experiment showed that, even in the presence of direct polar conjugation, the difference between the experimental and calculated dipole moments does not exceed 1–1.5 D. Furthermore, an analogous interaction occurs also in benzoylphosphine oxide and benzoylphosphinates, for which the results obtained by the dipole moment and infrared spectroscopic methods are virtually identical. It would be very useful to apply another independent method to this problem.

IV. THE CONFORMATION OF ARYL DERIVATIVES OF FOUR-COORDINATED PHOSPHORUS

The internal rotation of the hydrocarbon groups does not affect the magnitude and direction of the molecular dipole moment in terms of the approximation of the additive scheme. Their steric orientation may be established on the basis of molar Kerr constants (*mK*).[2] The first compound with the $C_{sp^2}{-}P^V$ bond investigated by this method was triphenylphosphine oxide[38]. The additive scheme for the anisotropy of the phosphorus bond polarisability has been analysed[2]. The available literature data show that one aryl group linked to the phosphorus atom (both tervalent and quinquevalent)[76,91] is located in the plane incorporating the axis of the CPX_2 (X = R or Hal) pyramid, i.e. is coplanar with the hybridised LEP of the phosphorus atom or with the phosphoryl group (Fig. 1).

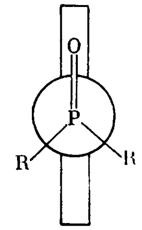


Figure 1. Conformation of dialkylarylphosphine oxides[91].

However, the aryl group in *p*-substituted arylphosphonates[23] is to a large extent displaced from the C_{sp^2}–P–O plane. Two regions of energetically favourable positions with rotation away from this plane to one side or the other ($\varphi = \pm 50°$), resembling the eclipsing of single P–O bonds (Fig. 2), have been observed for this group. It is of interest that, in the study of complexes of *O,O*-diethyl phenylphosphonite with different metals, a non-planar structure was also discovered ($\varphi = 55$–$75°$).[92] Thus the conjugation in *p*-substituted arylphosphonates[24] apparently cannot be of the π–π type and is better explained by a $p\pi$–$d\pi$ interaction. The conjugation between the phenyl and P=O groups has been confirmed by a study of the infrared spectra of cyclohexylphenylphosphine oxides.[93] The rotation about the P–C_{sp^2}(phenyl) bond in 2-oxo-(thiono)-2-phenyl-1,3,2-dioxaphosphorinanes (CII) and (CIII) and their spiro-analogues (CV) and (CVI) has been investigated[27], and it has been found that the conformer with an equatorial phenyl group predominates in these compounds (80%), the plane of the benzene ring being parallel to the LEP of the phosphorus atom or the P=O and P=S bonds. The plane of the benzene ring in the conformer with an axial phenyl group is perpendicular to the molecular symmetry plane in derivatives of both three- and four-coordinated phosphorus.

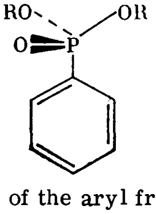


Figure 2. Orientation of the aryl fragment in *O,O*-dialkyl arylphosphonates[23].

The rotation of two aryl groups in OPC has been examined in relation to propynyl and trichloromethyl-diphenylphosphine oxides[33,40]. The angular variation of the calculated Kerr constant for compound (CLI) is very pronounced (Fig. 3), which made it possible to determine the conformation of this compound with a high accuracy. Owing to their linearity, the P=O bond and the P–C≡C group gives rise to the same steric hindrance to the rotation of substituents at the phosphorus atom; nevertheless a structure obtains in which the planes of the phenyl groups nearly eclipse the C≡C bond.

The experimental values of *mK* for diphenyltrichloromethylphosphine oxide (CXXII), trichloromethylditolylphosphine oxide (CXXIII), and di-*p*-chlorophenyltrichloromethylphosphine oxide (CXXIV)[33] correspond to the values calculated for an angle of rotation of 15°. Hence the conclusion that the conformations of the molecules investigated are close to the sterically least hindered conformation in which the plane of each aromatic ring is perpendicular to the C_{sp^2}–P–C_{sp^2} plane with a possible deviation by an angle up to 15°, which leads to the eclipsing of the phosphoryl group. The conformation established by Ishmaeva et al.[33] was explained by a balance between the energies of the steric interactions of the hydrogen atom in the *o*-position, within the pyramid formed by phosphorus bonds, with the analogous hydrogen atom in a neighbouring aryl group, on the one hand, and the trichloromethyl group, on the other. Thus the benzene rings in propynyl- and trichloromethyl-diphenylphosphine oxides are rotated by a small angle in different directions from the same initial position. However, in principle, similar results have been obtained for these compounds, i.e. the replacement of the linear propynyl group by the bulky trichloromethyl group has little influence on the conformations of the compounds.

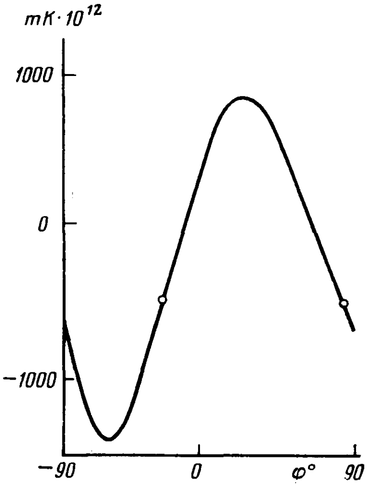


Figure 3. Conformational dependence of the Kerr constant for diphenylpropynylphosphine oxide (CLI)[40] (the circles on the curves represent experimental values).

The rotation of three aryl groups in triarylphosphine oxide molecules has been investigated[35,38,94]. Comparison of the experimental *mK* and the values calculated on the assumption of C_3 symmetry for unsubstituted triphenylphosphine oxide (CXXV) and its *p*-chloro-derivative (CXXVII), *m*-chloro-derivative (CXXIX), *p*-methyl-derivative (CXXXV), and *m*-methyl-derivative (CXXXVI)[35] led to the following angles of rotation of the benzene ring: 55°, 65°, 49°, 60°, and 52° respectively (Fig. 4). The halogen atom and the methyl group in the *p*-position lead to some flattening of the molecules compared with unsubstituted triphenylphosphine oxide. The authors[35] suggest that this may be accounted for from the standpoint of the $p_\pi - d_\pi$ conjugation of aromatic rings with the phosphorus atom. The possibility of a similar interaction has been pointed out in other studies[95,96].

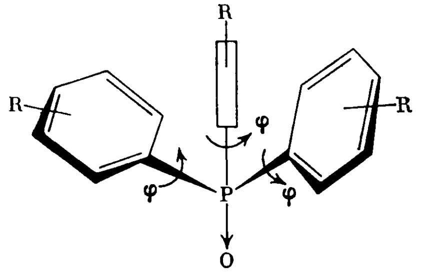


Figure 4. The conformation of triarylphosphine oxides[35].

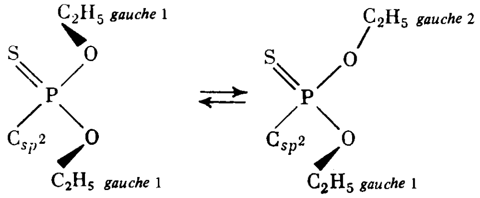
The data concerning the barriers to the rotation about the C_{sp^2}–P bonds are scanty. The rotational barriers have been estimated[87,97] from the torsional vibration frequencies of compounds (VII) and (XC): $V = 4-6$ kcal mole^{-1}.

V. CONFORMATIONAL ISOMERISM IN RELATION TO SINGLE BONDS IN UNSATURATED ORGANOPHOSPHORUS COMPOUNDS

It is now well known that, on rotation about single bonds in compounds of four-coordinated phosphorus, the *gauche*- or *trans*-form predominates[98-105], regardless of the bond (P–O, P–S, or P–Se) about which rotation takes place. Significant differences between compounds containing one, two, or three[106] irregular groups have not been observed. The same forms as in 2-alkoxy (methylthio, methylseleno)-2-oxo(thiono)-1,3,2-dioxaphosphorinanes[100,102,105] are produced in acyclic derivatives[104].

Data concerning conformational isomerism in relation to single bonds in unsaturated OPC are still very few[10,40]. However, they too indicate the preferred *gauche*- or *trans*-orientation to the alkyl and P=O or P=S group.

It has been found[10] that conformational equilibrium between two forms with the *gauche*-orientation of the alkyl and P=S groups (apparently with some distortion owing to a tendency towards the formation of the *cis*-form) obtains in diethyl vinylphosphonothioate (II):



As for diethyl ethynylphosphonate (CXLVI) and propynylphosphonate (CXLVII), the experimental dipole moments agree with the values calculated for structures with the *gauche*-disposition of the alkyl and P–O groups[39].

The study of the rotation about the C_{sp^3}–P bond in diethylpropynylphosphine oxide (CL) by the method based on the Kerr effect[40] led to the conclusion that the C–CH_3 bonds in the ethyl groups are only in the *gauche*-positions relative to the P=O group (Fig. 5). The experimental value $mK = -176 \times 10^{-12}$ for (CL) is rigorously consistent with calculations for the *gauche*$_1$, *gauche*$_1$-conformation (-180×10^{-12}) and the *gauche*$_1$, *gauche*$_2$-conformation (-178×10^{-12}). Analogous data for the structures of irregular methoxy-groups have been obtained for arylphosphonates[23]. A conformational equilibrium of the two forms of the above compounds has been demonstrated by infrared spectroscopy. These forms have been identified by the dipole moment method; the calculated and experimental data were treated by Exner's method[107], which led to the conclusion that the *gauche*-orientation of the methyl and P=O groups is preferred, with some distortion (up to 20°) towards the *cis*-form. The possibility, in principle, of such distortion has been confirmed also by quantum-chemical calculations[108].

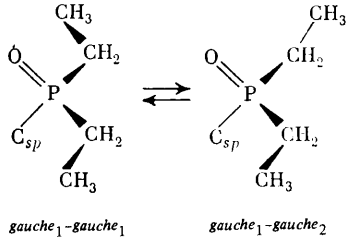


Figure 5. The orientation of the methyl groups and the P=O bond in the molecule of diethylpropynylphosphine oxide (CL).[40]

The rotation about the P–O bond in alkyl and aryl methylphenyl- and diphenyl-phosphinates[28,29] leads to conformers with the *gauche*-orientation of the alkyl or phenyl and phosphoryl groups. It is believed[28] that the increment in the refraction of the C_6H_5–P^V group (1.0 cm^3) arises owing to the conjugation of the benzene ring with the P=O group, while the second benzene ring, linked to the phosphorus atom, does not give rise to an analogous effect[28]. The *gauche*-orientation is preferred also in the esters of diphenylphosphinodithioic acid (CXI), di(*p*-chlorophenyl)phosphinodithioic acid (CXIV),[31] and di(*p*-chlorophenyl)phosphinodithioic acid (CXVI).[31]

Thus rotation about single P–O, P–S, and P–C_{sp^3} bonds in unsaturated OPC containing a four-coordinated phosphorus atom obeys rules common to organophosphorus compounds.

Summarising the discussion of the steric and electronic structures of unsaturated OPC with a four-coordinated phosphorus atom, one may note that the phosphorus atom is involved in a mesomeric type interaction. The steric orientation of the π-electron system is evidently to a large extent determined by these interactions, while the relative stabilities of the conformers involved in the equilibrium are controlled by polar factors. The presence of π-electron systems has hardly any influence on the conformations of the irregular groups attached to the phosphorus atom, which permits a comparison of the physical and chemical properties in large series of organophosphorus compounds.

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New Possibilities and Chemical Applications of Raman Spectroscopy

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The problems involved in the study and applications of Raman spectroscopy are considered, attention being mainly concentrated on resonance Raman spectroscopy. Theoretical studies are briefly surveyed and the applications of the method in the investigation of molecular structures and the mechanisms and kinetics of chemical reactions are discussed. Examples of the study of various organic, organometallic, and other compounds, polymers, haemoproteins, nucleotides, etc. are presented. The possible applications of the excitation spectra of resonance Raman lines are noted.
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I. INTRODUCTION

Raman spectroscopy is widely used in chemistry, physics, and other branches of science as one of the most important methods for the investigation of molecular structure. The set of characteristic vibration frequencies determined from the spectra together with intensity data for Raman lines yield information about the force constants of chemical bonds, molecular symmetry, the presence of definite structural groups in the molecule, and the interaction of these groups with one another. Raman spectroscopy makes it possible to determine the compositions of fairly complex products and helps to determine the structures of new compounds and to elucidate the mechanisms of chemical reactions[1-8].

However, in the first stages of the development of the method, its scope was limited to fairly severe conditions. Practical experience showed that the Raman effect may be excited by monochromatic light of any wavelength, provided that it lies in the range where the test substance is completely transparent (i.e. is remote from absorption bands). The substance scatters only a small proportion of the incident light (less than one thousandth under laboratory conditions); furthermore, almost the entire scattering is of the undisplaced (Rayleigh) type, while Raman scattering, which carries the most interesting information about molecular properties, constitutes only a few per cent of the total. Bearing in mind that less than one ten thousandth of the light scattered in all directions can be directed to the measuring apparatus (spectrometer), it is easy to imagine how small are the measured light fluxes of the individual Raman lines. In practice they can be observed only for high concentrations of the substance ($> 1\%$).

In attempts to excite the Raman effect in coloured substances in the region of absorption bands, virtually complete reabsorption occurred and the Raman lines were lost. It was suggested that under these conditions Raman scattering must be converted into fluorescence. Further theoretical studies showed that the transition to fluorescence is possible, but only in specific instances. On excitation by narrow spectral lines in the region of a fairly broad absorption band, typical Raman scattering should occur and be characterised by very high molar intensity coefficients[9].

In order to observe this effect, it was necessary to modify somewhat the usual experimental conditions; thereby it was possible to obtain distinct spectra of intensely coloured compounds. Thus, as early as 1948,[10] the Raman spectra of *p*-nitroaniline solutions were obtained with excitation in the violet part of the spectrum (within the half-width of the very intense band associated with the $\pi \rightarrow \pi^*$ electronic transition). Later the spectra of potassium *p*-nitrophenoxide were obtained with excitation at the absorption band maximum[11]. The intensity coefficients of the Raman lines were so high that the spectra were obtained without difficulty at concentrations $< 0.001\%$. The phenomenon described was called the resonance Raman effect[12].

Further studies demonstrated the possibility of observing the resonance Raman effect in chemical compounds of different classes[1]. Many objects, which previously could not be investigated by Raman spectroscopy, began to be studied with a fair degree of success. Measurements of the spectra of coloured liquid, gaseous[13-16], and solid substances were described, namely amorphous[17,18] and crystalline (semiconductors[19-24], non-conductors, various polymers[25,26], and minerals[27]) substances, monomolecular layers[28,29], chemical reaction intermediates present in solutions, free radicals[30-34], impurity centres in crystals[35-43], molecules in solid matrices[44-48], molecules in an electronically excited state[49], and compounds in natural systems (in the living tissues of plants and animals)[50-52]. One may note successful attempts at selective investigation of the structures of particular fragments of very complex molecules in whole erythrocytes[53], in the retina of a functioning eye[54], in bacteria[55,56], in viruses[57], etc. The spectra of a number of metals and metal compounds[58,59], wood charcoal, carbon black, etc. have been obtained[60]. The study of the resonance Raman effect promoted the solution of important problems of the interaction between light and matter and the elucidation of relations between principal molecular-optical phenomena[1,9].

The development of resonance Raman spectroscopy led to the establishment of an extensive branch of science within the limits of which new research fields began to be initiated; outwardly this was reflected by the appearance in Journals of new terms: "resonance Raman photochemistry",[61] "resonance Raman spectro-electrochemistry",[62-64] "internal reflection resonance Raman spectroscopy",[65] "X-ray resonance Raman spectroscopy",[66] etc.

Hitherto we spoke mainly of light scattering by molecules accompanied by excitation of molecular vibrations. The experimental observation of resonance rotational[67-69] and electronic[70] Raman light scattering by molecules, the electronic resonance Raman effect excited by X-rays in atoms[66,71,72], resonance scattering with spin-flip[4,73] and with excitation of magnons (spin waves)[74,75], excitons, and phonons (collective atomic vibrations in the crystal lattice)[76-83], and resonance-stimulated[84-87], inverse[88-90], and coherent[91-94] Raman scattering has been described in the literature in recent years. A sharp increase of the probability of Raman scattering and an increased applicability of the relevant methods to the study of molecules, crystals, and natural and technical products was noted in all cases.

Considerable progress in the experimental technique greatly extended the range of problems susceptible to solution by Raman spectroscopy. For example, the measurement of the spectra of atoms at the instant of collision in the gas phase, of individual optically active components of racemates, of flames, and of streams of exhaust gases from a reactive engine, accurate determination of the moments of inertia of molecules with revision of interatomic distances, and the study of the vibrational energy distribution of molecules formed in chemical reactions, of the distribution of electron densities in different parts of a single crystal, of the orientation of molecules in polymer blocks, etc. have become possible.

Delhaye[5] (Schmid., pp. 747 and 762) reported successful experiments involving the measurement of the Raman effect within 10^{-10} s, which gives rise to interesting prospects for the investigation of unstable species and the kinetics of rapid reactions (we may recall that at one time exposures lasting several minutes were regarded as a major achievement). A method has been developed for obtaining the images of microscopic objects at wavelengths of specified Raman lines ("micro-Ramanography"), which makes it possible to characterise the distribution of particular inclusions in homogeneous objects and to follow the chemical reactions in the latter.

Apparatus for measurements at a distance and for the investigation of remote objects under laboratory and field conditions (for the determination of flame temperatures, of the contamination of the atmosphere and water in the ocean, etc.) has been described. Ways of employing the method in astrophysics have been outlined and the parameters of Raman spectra have been used in the study of the atmosphere and in the determination of the geometrical albedos and diameters of planets on the basis of a determination of the rotational-vibrational satellites of Fraunhofer absorption lines arising in the scattering of the sun's rays by the planet's atmosphere[95-97].

The use of resonance excitation of the Raman effect has potential for a considerable improvement of the sensitivity and selectivity of the methods enumerated above.

As a result of the improvement of the experimental technique, many difficulties in the observation of the resonance Raman effect (for example, interference due to fluorescence) can be eliminated or reduced. Apparatus employing ultraviolet radiation has greatly extended the range of chemical compounds susceptible to resonance excitation. Thus nucleotides[98,99], simple amines, amides, dienes[100-103], benzene[104], etc. were investigated. Sources of monochromatic radiation with a smoothly adjustable frequency have created a considerable scope for the measurement of the excitation spectra of Raman lines, i.e. curves defining the dependence of Raman line intensities on the frequency of the exciting light $I(\nu)$. The study of excitation spectra, which may be regarded as a new and important branch of resonance Raman spectroscopy, has given rise to considerable possibilities for the investigation of molecules not only in the ground state but also in excited electronic states[9,105,106].

Below we shall briefly consider the main lines in the development of the theory of the resonance Raman effect and the chemical applications of the method. Problems closely related to those considered here have been considered in the past few years in certain specialised reviews (problems of conjugation[1], problems of the theory of the resonance Raman spectroscopy of molecules[9,107,108] and crystals[109,110], experimental investigations and technique[111], and the applications of the resonance Raman effect in biochemistry[112,113]).

II. ADVANCES IN EXPERIMENTAL TECHNIQUE

During the initial period of the study of excitation spectra, it appeared appropriate to employ three–four wavelengths in order to characterise $I(\nu)$ approximately in the region of broad absorption bands in the visible part of the spectrum. The development of tunable lasers made it possible to cover the range 3000–7000 Å with any required number of points and to obtain information about the $I(\nu)$ relation, including the regions of the fine structure of the absorption spectrum, where a series of extrema were recorded with intervals smaller than 1 cm^{-1} for varying excitation frequency ν.[114] Indirect methods for characterising the excitation spectra (employing the change in the positions of absorption bands with variation of the composition of binary systems[76,116], the solvent[115,116], the temperature of the substance[17,77], the pressure, etc. at a fixed frequency ν) have now become of secondary importance.

The use of very short exciting light pulses (10^{-11}–10^{-8} s) and the recording of secondary resonance radiation with time scanning and separate observation of synchronous glow and afterglow are of exceptional interest. The pulse technique has been used, on the one hand, to study the mechanisms of the resonance transformation of light by molecules[117] and, on the other, to investigate short-lived intermediates by the resonance Raman method[118].

Excitation in the region of absorption bands may give rise to considerable experimental difficulties from the large light losses in the specimen and the photochemical decomposition of the substance. The light losses are reduced to a minimum by optimising the concentration of solutions (this was used already in the first observations of the resonance Raman effect[11] and has been specified in detail[119,120]) or by reducing the optical path length in the absorbing medium with selection of light scattered by surface layers of the specimen in the direction opposite to that of the incident light[121]. In another version the light beam is directed through a transparent plate or layer of liquid at a low angle onto the interface with a coloured solution[27,122]; the reflected light is enriched in the spectral components of the light involved in resonance Raman scattering as a result of the interaction of the incident light with the molecules in the surface layer of the coloured substance. The distribution of surfactants in a monomolecular layer at the interface with respect to molecular orientations was characterised by a similar method[28].

The interference due to the photochemical decomposition of the substance is reduced by scanning the incident light beam over the surface of the specimen[123], by rapid rotation of the cuvette[111], or by employing a flow technique[124-127]. For a flow rate of 1–10 m s^{-1}, which is readily attainable, it is possible to obtain distinct resonance Raman spectra of relatively unstable products[128]. The kinetics of the rapid reaction between horseradish peroxidase and hydrogen peroxide have been studied in this way[129]; the resonance Raman spectra were recorded a fraction of a second after mixing the reactants and the start of the reaction and at long time intervals; by selecting a particular zone along the length of the stream it was possible to detect the formation of unstable intermediates and to characterise the kinetics of their decomposition.

The interference due to fluorescence may be eliminated by employing a series of procedures: 1. By adding quenching agents (for example, nitrobenzene)[130,131]. 2. By modulating the polarisation of the incident radiation[132] and separating the polarised Raman lines from the depolarised fluorescence. 3. By modulating the frequency of the measured secondary radiation and recording the derivative $dI/d\omega$, whereby one can isolate resonance Raman lines which are narrower than the fluorescence lines; it is more effective[133] to modulate the frequency of the incident light, so that the positions of the fluorescence bands are not modulated, (in contrast to those of the Raman lines) and the receiving device does not record them[134]. 4. By illumination with short pulses combined with synchronous recording of the secondary radiation but not the afterglow[111,135]. 5. By carrying out measurements in the anti-Stokes region (see Section IV). 6. By ensuring the maximum monochromatisation of the incident light.

III. THE RESONANCE RAMAN EFFECT WITH EXCITATION OF ATOMIC VIBRATIONS

The resonance Raman light scattering by molecules, which takes place with excitation of atomic vibrations, has been most thoroughly investigated and has found extensive applications in chemistry and physics. The resonance conditions arise when the frequency of the incident light ν is in the region of the absorption band of the substance corresponding to the $0 \rightarrow e$ electronic transition. Such bands are usually located in the visible or ultraviolet regions; for many compounds in the vapour phase they have a fine vibrational-rotational structure but are very broad for solutions (500–5000 cm^{-1}). On irradiation with quasi-monochromatic light, the secondary radiation includes that produced by the resonance Raman effect in the form of narrow lines and possibly (cf. Ref. 136) fluorescence bands, which are usually just as broad as the absorption bands[137,138]. In those cases where the fluorescence spectrum consists of narrow lines, the latter may be mixed with the Raman lines[45,139-145], hindering the interpretation of the spectrum; the broad fluorescence bands interfere with the recording of the Raman scattering.

Resonance excitation does not modify the observed vibrational frequencies ω and the contours of the Raman lines, but increases the line intensities by several orders of magnitude[9-11,144,145]. On the other hand, the quantum yield of the Raman scattering[146] changes only slightly and remains very low[126,147-150]; for aromatic nitro-compounds in solution, it amounts to about 10^{-8} and depends comparatively little on the properties of the solvent and temperature (this cannot be said of fluorescence)[137,138].

Table 1 presents as an example the parameters[137] of the usual fluorescence (including the afterglow time τ_e) and the lines due to the nitro-group in the resonance Raman spectrum of 4-dimethylamino-4′-nitrostilbene after excitation with light in the region of the maximum of the $\pi \rightarrow \pi^*$

broad absorption band (~ 23 000 cm^{-1}); I^s is the molar intensity coefficient of the Raman line[1].

In successive experiments with excitation using light corresponding to different $0 \rightarrow e$ bands of the same substance, it is possible to observe resonance-induced intensification of various sets of Raman lines[79-81,151-154], preferentially those corresponding to fully symmetrical vibrations. The similarity between the locations (and orientations) of the electronic and Raman transitions is then important[128,155,156,184]. For example an intensification of the Raman lines due to the Co–N bond in the $Co(NCS)_4^{2-}$ ions was noted when the frequency ν was in the range corresponding to the band associated with the electronic excitation of Co–N bonds and an intensification of the C–N and C–S lines was observed on excitation of the Raman effect in the region corresponding to the short-wavelength absorption band due to the electronic excitation of the ligands[157]. Ultimately, everything depends on the electronic transitions which are influenced by particular atomic vibrational modes (see Section V). The electronic transitions which make a significant contribution to the intensity of a Raman line are said to be "effective" for this line[144,158]. However, this term was subsequently frequently used with another significance—implying a "centre of gravity" of the contributions of different transitions (this interpretation is permissible for Rayleigh scattering but hardly for Raman scattering, where the contributions of different levels may have different signs!).

Table 1.

Solvent	Fluorescence		Resonance Raman effect	
	quantum yield	τ_e, s	ω, cm^{-1}	I^s
Benzene	0.7	$3 \cdot 10^{-9}$	1340	5000000
Acetone	<0.03	$<10^{-10}$	1338	6000000

The lines due to the Raman overtones ($\nu - k\omega$) under conditions remote from resonance are so weak that they are rarely susceptible to observation. However, as resonance is approached, their intensity may increase sharply—to a greater extent the higher the order of the overtone k and they may form a complete progression[9,159,160]; this is possible for those fully symmetrical atomic vibrations which modulate the electronic transition frequencies ν_e.[9,161-163] Such progressions were observed for the first time in the resonance Raman spectra of diphenylpolyenes[138] and subsequently of many other compounds[164-166]; thus fifteen overtones have been observed in the spectrum of I_3^- ions[42] and 25 in that of iodine[142,167]. If the decay of the electronic oscillator is rapid, then Rayleigh scattering continues to predominate in the resonance spectrum with a smooth decrease of intensity within a series of $k\omega$ overtones[9,156,168-172] (and with a gradual broadening due to the broadening of the rotational and isotopic structures and finite vibrational k states[42,173-177]; see, however, Howard and Andrews[178]). In other cases the smoothness of the decrease may break down[9,179-182].

The measurement of the frequencies of the resonance Raman overtones led to new possibilities for the determination of the coefficients of the mechanical anharmonicity of the vibrations[142,156,170,176] and for the revision of the frequencies and the force fields in molecules[183]; data were obtained for metal–metal[156,184], metal–halogen[160,185], etc. bonds.

The lines of the non-totally symmetric ω_{as} vibrations proved to be the most intense in the Raman spectrum only in very rare instances; this has been observed for pyrazine on excitation with light at wavelengths in the vicinity of the $n \rightarrow \pi^*$ band[186], certain metalloporphyrins on excitation with light corresponding to the long-wavelength $\pi \rightarrow \pi^*$ band[187-191], and a few other compounds[192-196]. According to Kettle et al.,[197] the high ω_{as} intensity for $Mo(CO)_6$ can be accounted for by the fact that, when the CO bond is extended, the polarisability increases along the bond and decreases at right angles to it. However, there is no doubt that the symmetry properties of the resonance level e are of primary importance. Progressions in $k\omega_{as}$ overtones have not been observed experimentally, although in principle they are not ruled out in the presence of a high anharmonicity and for large differences between the shapes of the $E(Q)$ potential energy curves for the ground and excited electronic states; in a few isolated instances it has been possible to observe a single $2\omega_{as}$ overtone in the resonance Raman spectrum[198-200].

Another characteristic feature of the resonance spectra is the possibility of the appearance of vibrational line with inverse (degree of depolarisation $\rho \rightarrow \infty$) or anomalous ($3/4 < \rho < \infty$) polarisations. These include the very intense lines of certain non-totally symmetric a_{2g} vibrations in the spectra of metalloporphyrins with D_{4h} symmetry (vibrations with turning motions of the atoms of the macroring)[190,201]; for other examples, see Refs. 202–207.

Inverse polarisation implies that the oscillating dipole induced by the electric field of the light wave along the direction of the field (x) is not modulated by the vibrations of the normal nuclear coordinate Q and does not contribute to the Raman effect, while the y-component at right angles to the field is modulated and gives rise to a Raman line. For this unusual situation to occur, the "vibronic interaction" (see Section VI) is not obligatory (cf. Refs. 208–210). We shall consider an example in a very simplified form. Two identical electronic oscillators rock slightly in the course of the intramolecular vibrations of atoms with retention of mutually perpendicular orientations[211] of the dipole moments of the $0 \rightarrow e$ transitions (see Fig. 1, the vectors M). The resultant x-component of the vibrations of the two electronic oscillators is then high but virtually unmodulated. On the other hand, the y-component is on average zero, but under certain conditions it may be actively modulated by the atomic vibrations; the extent of modulation is determined by the sum of the projections of two vectors corresponding to the change in the orientations (ΔM) and two vectors corresponding to the change in the amplitudes (δM) of the oscillations (caused by the change in the effective field). When the decay constant of the electronic oscillator is high ($\gamma_e > \omega$) or when the Raman effect is excited under conditions remote from resonance, the modulation of the orientations and amplitudes of the oscillations of the electronic oscillators takes place in phase and the sum of the four ΔM and δM vectors is close to zero; when $\gamma_e < \omega$ the phases of the modulation of the orientations and amplitudes of the oscillations do not coincide, as a result of which the annihilation of the four ΔM and δM

modulation components is disturbed; the spectrum of the y-component vibrations then contains the $\nu \pm \omega$ frequencies, i.e. Raman lines, although the ν frequency is absent.

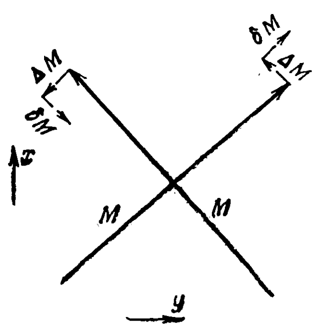


Figure 1. Evolution of the dipole moments of the transition in the course of atomic vibrations (model of a molecule with D_{4h} symmetry).

Anomalous polarisation has come to be invoked for the assignment of the resonance Raman lines to symmetry species[202,212,213], and to determine more precisely the symmetry of systems of conjugated bonds[151,190,214] and electronic transitions[204]. However, when the frequency ν changes, the quantity ρ for certain lines of porphyrins and other compounds[205,215] changes from values characteristic of fully symmetrical vibrations ($< 3/4$) to larger values ($\gg 1$), which has not so far been adequately explained and has complicated the assignment of the lines. Additional data for the $\rho(\nu)$ relation may be found in a number of studies[216-221].

Thus the resonance Raman effect is characterised by very high intensity coefficients and in certain cases also by the appearance of progressions of overtones; in a few instances there is a possibility of the appearance of anomalously polarised lines.

The resonance Raman effect may be regarded as absorption of an $h\nu$ photon and simultaneous emission of an $h(\nu \pm \omega)$ photon with an altered energy. The concept of absorption, the intermediate excited state of the molecule, and emission as successive stages of the transformation of the photon corresponds to the resonance fluorescence process and has been invoked to describe the Raman effect[222, 223] in purely conventional terms.

Typical scattering differs from the usual (relaxed) and resonance fluorescence by the following features: (1) the shift of the exciting light line in the spectrum induces the same shift of all the Raman lines (cf. Ref. 67); (2) the width of each Raman line is determined mainly by the width of the exciting line but not by the contour of the absorption band[9,224] (cf. Ref. 225); (3) there is no afterglow and no rotational depolarisation (cf. Ref. 117, where a different terminology is used).

Resonance fluorescence may be excited under the conditions of exact resonance ($\nu = \nu_{ev}$) for a very narrow absorption band (for $\gamma_e < \Gamma$, where Γ is the half-width of the incident light band). Radiationless deactivation of the intermediate excited state of the molecule[226] leads to a broadening of the absorption band, to a decrease of the intensity of the secondary resonance emission (Schmid[8], p. 286), and to its modification as far as transition to typical scattering when $\gamma_e \gg \Gamma$. Thus it creates conditions for the occurrence of scattering while at the same time it behaves as a competing process.

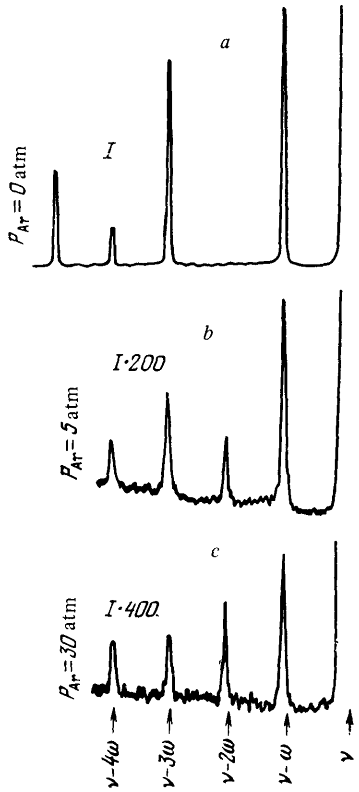


Figure 2. Spectra of the secondary emission of iodine vapour in the presence of argon; excitation by the 5017 Å line in the region of the discrete iodine absorption spectrum. With increase of argon pressure p_{Ar} from 0 to 30 atm, the intensity of the secondary emission falls sharply and there is a gradual transition of the intensity distribution in a series of overtones from that characteristic of resonance fluorescence to a smooth decrease of intensity characteristic of resonance Raman spectra[181].

The possibility, in principle, of a smooth transition from typical light scattering to resonance fluorescence with a gradual alteration of the difference $\nu_e - \nu$ and of the relations between the half-width of the incident light band Γ and the molecular parameters γ_e, ω, and the rotational frequency Ω has already been mentioned in a review[1]. Brilliant experiments, demonstrating the reality of the gradual disappearance of the dependence of the secondary emission line frequency on the frequency ν,[227] of the change in the energy distribution in the series of $0 \rightarrow k$ overtones (Fig. 2)[181], and of the evolution of the rotational structure of the lines with transformation of the Q-branch of the resonance Raman line into the R-branch of the resonance fluorescence line (Fig. 3) were carried out recently[14,181].

Certain data concerning the transformation of scattering into fluorescence as the resonance conditions are approached ($\nu = \nu_e$) for NO_2 and naphthalene and pyrazine crystals have been reported[228-230]. A resonance emission of an intermediate type, close to scattering, has been noted for solutions of diphenylpolyenes[138] and emission closer to fluorescence has been observed for ND_3 in the gas phase; in the latter case the half-width of the vibrational-rotational component of the absorption band (~ 2 cm^{-1}) was close to the half-width Γ of the incident light band[150].

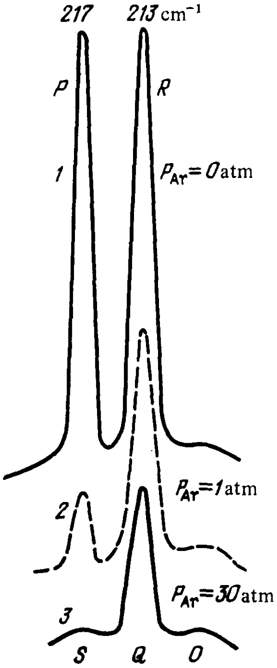


Figure 3. Modification of the rotational structure of the ~ 215 cm^{-1} iodine line with increased pressure of argon (transition from resonance fluorescence to resonance Raman spectra)[14]; the details have been omitted and the scale is arbitrary: 1) p_{Ar} = 0 atm, resonance fluorescence spectrum; 2) p_{Ar} = 1 atm, transitional spectrum; 3) p_{Ar} = 30 atm, resonance Raman spectrum.

Fig. 4 illustrates a very simplified example of the formation of the $I_{em}(\nu)$ secondary resonance emission spectrum in the region of a single $\epsilon(\nu)$ absorption band; the $I_{inc}(\nu)$ incident light line is shown continuous. The plot of the intensity of the secondary emission has two maxima; the left-hand and right-hand maxima symbolise resonance fluorescence and scattering respectively.

The problem of the boundary between scattering and fluorescence has been the subject of a lively discussion in the literature with invocation of various criteria[7,9,108,231-237].

IV. OTHER FORMS OF THE RESONANCE RAMAN EFFECT

Inverse Spectra

When light whose spectrum contains an intense ν line and a second component consisting of a broad band in a nearby region of the spectrum passes through a substance, weakening of the light flux may be observed predominantly in the region of the $\nu + \omega$ frequency (where ω is the frequency of the atomic vibrations in the molecule). This is because the "biharmonic" combination of the ν and $\nu + \omega$ components of the light field (which may be regarded as vibrations with beats at a frequency ω) may excite the atomic vibrations (along the normal coordinate Q) with a corresponding loss of light field energy provided that the derivative of the polarisability of the molecule $\partial\alpha/\partial Q \neq 0$. The components of the broad band, the frequencies of which are not equal to $\nu \pm \omega$, do not participate in such processes and are not weakened. The resulting selective (with respect to the spectrum) weakening of the light which has passed through the substance is called the "inverse Raman effect" or "inverse combination scattering" (although in essence it is not scattering). Resonance phenomena are observed for $\nu = \nu_e + \omega$ (when the intensity of the ω line increases) or when $\nu = \nu_e$ (when the intensities of all the Raman lines increase)[89,90].

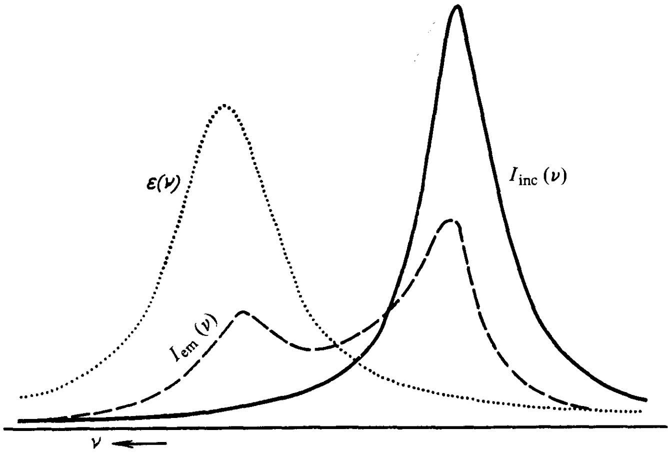


Figure 4. The $I_{em}(\nu)$ secondary emission spectrum (dashed line) with the oscillator vibrations excited in the vicinity of resonance (the simplest oscillator model); $\epsilon(\nu)$ absorption spectrum.

Coherent Active Raman Spectroscopy

When $\partial\alpha/\partial Q \neq 0$, a biharmonic light field, incorporating the ν and $\nu + \omega$ frequencies, is capable of exciting in the molecules of the given substance atomic vibrations which are concerted as regards phase over a fairly large volume of the specimen. The additional monochromatic excitation with a frequency ν^* is then actively modulated by these vibrations and gives rise to narrow directional beams due to displaced "scattering" at a frequency $\nu^* \pm \omega$ with a very large quantum yield. This phenomenon can also be regarded as a kind of refraction of light. When $\nu^* = \nu_e$, conditions are created for the resonance transformation of light, which has been demonstrated for iodine vapour[91] and solutions of β-carotene[92] and other compounds[93], (Schmid[5], p. 740). The high intensity of the anti-Stokes ($\nu + \omega$) lines make it possible to investigate the Raman spectrum in the region where the interference due to fluorescence is a minimum.

The Resonance Raman X-Ray Scattering by Metal Atoms

This has been observed under conditions where the energy $h\nu$ (reaching 9000 eV) was close to the K-electron ionisation energy[66,71,72]. Under these conditions, the absorbed photon causes the transfer of an electron from the K-shell to the conductivity band, while an electron from the L-shell fills the resulting vacancy in the K-shell, which is accompanied by the emission of a resonance Raman effect photon; the final state of the atom is determined by the presence of an additional electron in the conductivity band and of a vacancy in the L-shell.

For details about the possible applications and other forms of the resonance Raman effect, see the literature quoted in Section I. A common feature of all types of the resonance Raman effect is the high probability of the transformation of photons and the high sensitivity of the methods.

V. PRINCIPAL TRENDS IN THE DEVELOPMENT OF THE THEORY OF THE RAMAN AND RESONANCE RAMAN EFFECTS

Various aspects of the theory of the Raman effect excited under conditions close to and remote from resonance have developed vigorously in recent years. Firstly, the ideas concerning the mechanism of light scattering by molecules with excitation of vibrational and rotational states have been extended and specified in greater detail. A tendency has arisen to establish quantitative relations between the Raman line intensities and other physical and chemical properties of the molecule. Secondly, new fields and methods have been described (for example, the method of differential spectroscopy). Significant advances have been made in all these aspects of the theory.

The intensity of the mth Raman line excited by a monochromatic light flux of constant and moderate intensity can be determined from the set of all the Cartesian components of the derivative of the polarisability with respect to the normal nuclear coordinate $\partial\alpha/\partial Q \equiv \alpha'$; without going into details, one can assume that the intensity is proportional to $(\nu - \omega)^4|\alpha'|^2$. In the simplest version of the semiclassical theory[1,9,144] the quantity α' consists of contributions by all the levels (e) of the electronic excitation of the molecule:

$$\alpha' = \mathrm{const}\cdot\sum_e\left[\frac{f'_e}{z} - \frac{2f_e\nu_e\nu'_e}{z^2}\right] = \sum_e (b^*_e + a^*_e) \tag{1a}$$

or

$$\alpha' = \mathrm{const}\cdot\sum_e\left[\frac{(M^2_e)'\nu_e}{z} - \frac{M^2_e(\nu^2_e+\nu^2)\nu'_e}{z^2}\right] = \sum_e (b_e + a_e), \tag{1b}$$

where $z = \nu_e^2 - \nu^2 + i\nu\gamma_e$, ν is the frequency of the incident light, M_e, f_e, and ν_e are the matrix elements of the dipole moment, the oscillator strength, and the $0 \rightarrow e$ electronic transition frequency, and γ_e is the decay constant; each level e is regarded as an integral hole (without taking into account the vibrational-rotational structure) and the frequency ν_e corresponds to the absorption band maximum; here and henceforth a prime denotes derivatives with respect to Q. The terms b_e (or b_e^*) are determined by the modulation of the values of M_e (or f_e) by the atomic vibrations and the terms a_e (and a_e^*) are determined by the modulation of ν_e; the latter arises when electronic excitation entails a change (Δ_e) in the equilibrium interatomic distances and Q.[1] Non-totally symmetric vibrations (for which $\Delta_e = 0$) cause the modulation of the M_e (or f_e) values only (if one disregards local electronic excitations), but for overtones both mechanisms of the modulation of α are important. The intensity of the overtones[238] is determined by the highest derivatives of α with respect to Q.

A method for the determination of the mechanism of modulation, employing a more marked dependence of the Raman line intensity on the frequency ν under the conditions of the modulation of the electronic transition frequency ν_e, was proposed a long time ago[239,240]. Despite the imperfection of the experimental technique, it was then possible to show that both types of modulation, i.e. both terms, a_e and b_e, may play an important role and that, as resonance is approached, the relative importance of the a_e term increases[145,240]. Little reliable information has yet been obtained on these problems. Some workers[6,241] do not take into consideration the a_e terms [the reasons for this being stated (or not)[134] with reference to an experiment, or to intuition[242]].

Incidentally the term a_e has not been entirely correctly transformed into the expression $[1 + (\nu/\nu_e)^2][1 - (\nu/\nu_e)^2]^{-2}$ and has been used in this form[243-248] to extrapolate α' to $\nu \rightarrow 0$ (according to the authors[248,249], this leads to a "more correct" value of α').

Eqns. (1) can be regarded as the result of certain simplifications in the Kramers–Heisenberg–Weisskopf formula. The latter has also served as the basis of a number of other versions of the theory. The appreciable differences in the formulation of the fundamental expressions and the contradictory estimates of the role of different factors as well as inaccuracies and errors in individual instances may make it difficult to become acquainted with the extensive relevant literature; certain explanations are therefore useful.

The familiar Albrecht formula in its initial form[250] took into account, like the Placzek polarisability theory (despite the assertions of Chao and Lippincott[241] and Schulman and Detrano[251]), only the modulation of M_e, i.e. the factor M'_e (the term b_e). Later[252] account was taken also of the modulation of ν_e (the factor ν'_e, the term a_e) and a more complete agreement with Eqn. (1) was achieved. The origin of the dependence of M_e on Q, i.e. of the derivative $\partial M_e/\partial Q = M'_e$, was specified in greater detail on the basis of the idea that the wave functions φ of different electronic excitation levels e and s are mixed on passing from the equilibrium configuration of the molecule ($Q = 0$) to the non-equilibrium configuration ($Q \neq 0$) during atomic vibrations ("vibronic interaction"[31,222,250,252-255]). The coefficients of the mixing of the wave functions h_{es} are specific to each vibrational mode; it has been suggested[256-258] that h_{es} should be greater the larger the alteration in the frequency ω on electronic excitation.

We shall elucidate the above statement concerning the "vibronic interaction" by a simple example. We shall assume that, for the equilibrium positions of the atoms, the $0 \rightarrow e$ electronic transition is forbidden; on deformation of the molecule by the nth normal vibration (i.e. for $Q_n \neq 0$), the wave function φ_e is modified as a result of the "admixture" of the wave function of another electronic level s, the transition to which ($0 \rightarrow s$) is allowed; the oscillator strength f_e for the deformed molecule will then prove to be non-zero and during atomic vibrations the "admixture" of φ_s and the quantity f_e (and hence M_e) will be actively modulated, contributing to the intensity of the Raman line[250,264]. In the simplest case where only two electronic excitation levels e and s are involved and in the absence of the modulation of ν_e and ν_s, one must assume that $f'_e = -f'_s$; one then obtains from Eqn. (1) the multiplier

$$F_B = \frac{\nu_e \nu_s + \nu^2}{(\nu_e^2 - \nu^2)(\nu_s^2 - \nu^2)},$$

the square of which should describe, according to Ziegler and Albrecht[104,250], the $I(\nu)$ relation.

In the general case one must take into account the mixing of the φ for all the levels e and s. Thus, instead of the single quantity M'_e for a single level e in Eqn. (1), one should introduce the complete matrix of the coefficients h_{es}, which is particularly complex in the case of overtones, because it includes higher-order coefficients (cf. Refs. 222, 223, and 259). The problem has been simplified by Warshel and Dauber[260] in essence at the price of partial neglect of the mixing of the wave functions. A realistic estimate of certain coefficients h_{es} has been achieved in only isolated instances[254,257,261]. The quantities M'_e and f'_e can be determined, in principle, from the analysis of limited sections of the absorption spectrum and are known for many simple molecules[262]. Both procedures, with introduction of M'_e and the mixing coefficients h_{es}, may be useful in the study of the mechanism of the Raman effect. However, examination of the set of all the Cartesian components M'_e makes it possible to take into account not only the "vibronic interaction" and h_{es} but also the contribution of the turning motions of individual fragments of the molecule.

Formulae for specific instances of excitation before and after resonance and between two absorption bands have been obtained[241,242,263]. They correspond to neglect of the term a_e and the unjustified introduction into the initial expression of resonance denominators of the type $|\nu_e - \nu|$ instead of $(\nu_e - \nu)$ and cannot be treated as correct.

Like all other formulae where the level e is regarded as an integral whole, Eqns. (1) are suitable in the resonance region only for very high values of γ_e on excitation to the region of broad structureless absorption bands; in the presence of vibrational structure one must take into account the contribution of the individual sublevels v, which, generally speaking, can be achieved on the basis of both classical and quantum theories[9,239,264].

We shall make use of the latter and shall quote in a very simplified form the expression for the matrix element of polarisability, which facilitates the determination of the term-by-term correlations with Eqn. (1b):

$$\alpha_{0k} = \frac{2}{hc} \sum_e \left[M_e^2 \sum_v \frac{\nu_{ev} A_{0v} A_{vk}}{\nu_{ev}^2 - \nu^2 + i\nu\gamma_{ev}} + \sum_v \frac{\nu_{ev} B_{ev}}{\nu_{ev}^2 - \nu^2 + i\nu\gamma_{ev}} \right] = \sum_e (\mathrm{A}_e + \mathrm{B}_e), \tag{2}$$

where ν_{ev} is the frequency of the $00 \rightarrow ev$ vibronic transition (in cm^{-1}), A_{0v} and A_{vk} are the overlap integrals of the nuclear wave functions of the 00 and ev and of the ev and $0k$ sublevels, and $B_{ev} = \mathbf{M}_e^{0v} M_e^{vk} - M_e^2 A_{0v} A_{vk}$, where $\mathbf{M}$ (in contrast to M) have been constructed from the complete wave functions ψ and not from the purely electronic wave functions φ, the superscripts denoting the quantum numbers of the vibrational sublevels of the combining states. The quantities B_{ev} and B_e are associated with the coefficients of the expansion of M_e in a series in powers of Q or, in terms of a more drastic simplification, with h_{es} [see Krushinskii and Shorygin[264] as well as Eqn. (8) in the paper of Rousseau and Williams[117]]. The term A_e is, roughly speaking, proportional to Δ_e.

The intensity of the Raman line of the fundamental band ($k = 1$) is proportional to $|\alpha_{01}|^2$, the intensity of the first overtone ($k = 2$) is proportional to $|\alpha_{02}|^2$, etc. For the fundamental, the terms A_e and B_e corresponding to each level e approximately correspond to the terms a_e and b_e of Eqn. (1).

According to Eqn. (2), the line intensity reaches a maximum when the frequency ν coincides with any component ν_{ev} of the structured absorption band; the excitation spectrum then has a series of maxima, the intervals between which are equal to the vibration frequencies of the atoms in the electronically excited states (whereas in the Raman spectrum itself the intervals in the progression of $k\omega$ overtones are determined by the frequency ω of the atomic vibrations in the ground electronic state); for very small[265,266] shifts Δ_e (and for a small anharmonicity of the atomic vibrations in the electronically excited state), only two maxima remain in the vicinity of the frequencies ν_{e0} and ν_{e1} (for the first overtone, in the vicinity of ν_{e0} and ν_{e2}; cf. Ref. 267). In complex molecules one cannot rule out the possibility of the separation of the $I(\nu)$ maxima with frequencies ω of "foreign" modes[254,268].

Owing to the difference between the signs of A_{vk}, the contributions of the sublevels v to A_e have different signs[239], which leads to a more pronounced $I(\nu)$ relation for Raman lines compared with Rayleigh scattering, particularly in the case of overtones, where there is a possibility of a repeated alternation of signs in a series of v sublevels[9] (a similar result in the semiclassical theory is determined by the higher powers of the resonance denominators). The neglect[269,270] of the integrals A_{vk} or of the differences between their signs is unjustified.

The difference between the signs of the contributions of different electronic levels e is associated with the difference between the signs of Δ_e (and also M'_e).[239,264] For a specific frequency of the incident light, this can lead in individual instances to the "annihilation" of the contributions of different levels e with weakening or complete disappearance of the Raman line, i.e. to the appearance in the excitation spectrum of an "anti-resonance" band (see the data for naphthalene[200], CdS,[271,272] and other compounds[115,273,274]; cf. Refs. 275–277). The appearance of anti-resonance owing to the different signs of the terms A_e and B_e for a single level e has already been examined[264].

The calculation of the values of $A_{0v}A_{vk}$ for all the sublevels v is fairly complex[168,180,278-280]. In order to simplify the task, it has been suggested that the entire sum with respect to v [see Eqn. (2)] be expanded in a series[107,275,281] in powers of $\nu_e - \nu$; then[107] $\mathrm{A}_e \simeq [(\nu_e - \nu)^{-2} - \omega(\nu_e - \nu)^{-3} + \ldots]$. However, under conditions remote from resonance, this procedure leads to the same results as the more compact Eqn. (1) and in the region of resonance it gives rise to a diverging or a slowly converging series and loses its significance. The expansion[282] in powers of $\nu_{e0} - \nu$ gives rise to an even worse convergence. The above series[107] yields a more marked $I(\nu)$ relation for Raman lines with low frequencies which can actually occur only in certain special cases (approximately the same may be said about the $I \propto \omega^2$ relation obtained by Warshel and Dauber[260]).

Peticolas et al.[283] obtained a formula for the Raman intensity without summation with respect to v but with a resonance denominator of the type $(\nu_e - \nu)(\nu_e + \omega - \nu)$; in the region of a single electronic excitation level e it gives rise to two resonance points, ν_e and $\nu_e + \omega$, and therefore in the vicinity of resonance it is suitable only for a very low deformation Δ_e of the molecule on electronic excitation; the two resonance points then correspond to the frequencies ν_{e0} and ν_{e1}. The same may be said of the formulae of Kobinata[259] and Nafie et al.,[223] designed for the region of resonance, which cannot be justifiably applied to iodine molecules with their large value of Δ_e.

The employment of such formulae is more appropriate for crystals, where Δ_e is as a rule very low and a vibrational structure is not usually observed for discrete electronic levels. However, the latter led to certain other misunderstandings. The appearance of two maxima in the region of one level e (for $\nu = \nu_e$ and $\nu = \nu_e + \omega$) was interpreted as the manifestation of resonance with the incident photon ($h\nu$) and with the scattered[76,77,116,284,285] photon $h(\nu + \omega)$. In fact the usual resonance takes place, in the first instance with the purely electronic $00 \rightarrow e0$ transition, which is clearly visible in the absorption spectrum, and in the second case with the vibrational satellite corresponding to the $00 \rightarrow e1$ transition, which is very weak but which gives a high quantum yield for the Raman line. Double resonance[285-287] must be interpreted in the same spirit—as the resonance with two partly overlapping sublevels $e1$ and $s0$.

On excitation of the resonance Raman effect in the region of an absorption continuum, arising from an electronic transition to a repulsive state or a state with rapid decay, the line intensities may be determined from Eqns. (1) and (2) with the corresponding constants γ_e or by means of other[226,288-290] suitable variants, for example by integration of the contributions from all the elements of the profile of the continuum without the introduction of a decay constant (as is done in the determination of polarisability by the Kramers–Kronig method)[159,291-294]. In any case, the knowledge of the form of the $\epsilon(\nu)$ continuum is insufficient for the calculation of the resonance Raman intensity.

The above formulae describes the smooth increase of the Raman intensity as ν approaches the region of maximum absorption in the continuum and the decrease of intensity on further increase of ν. However, according to Laplante and Bandrauk[295], here there should be whole series of maxima with decrease of intensity between them down to zero. This conclusion is incorrect and arises from the use of ideas about the $E_e(Q)$ "potential energy curve" for the repulsive state without taking into account the effect of the uncertainty principle when the effective lifetime of the intermediate state τ_{eff}, which limits the time over which emission of scattered radiation with transition of the molecule to the $0k$ state can occur; this time is longer the smaller the slope of the $E_e(Q)$ curve for $Q = 0$.

Above we were concerned with the usual cases to which the adiabatic approximation is applicable. The influence of non-adiabatic conditions on the intensity of the resonance Raman effect and on the excitation spectra has been considered[107,296,297].

In order to calculate the intensities of Raman and resonance Raman lines for specific molecules by Eqns. (1) and (2), it is necessary to know a set of parameters, which can be determined, in principle, from electronic absorption spectra or calculated theoretically[9,260,298,299]. In more primitive versions of the theory semiempirical relations and simplified molecular models are introduced instead of Eqns. (1) and (2). Below we shall consider briefly the methods of calculation employed, which will be arranged in order of increasing research value and rigour.

Applequist and Quicksall[300] calculated $\partial\alpha/\partial Q$ for methyl halide molecules using the Silberstein theory, which has been known for a long time and which assumes that each atom X in the molecule is polarised directly by the electric field of the light wave and by the field of the dipoles induced by light at the neighbouring atoms Y—the "partners" in chemical bonds; this additional polarisation naturally depends on the interatomic distances $q_{\text{X-Y}}$, which is described by the increments $\partial\alpha_{\text{X}}/\partial q_{\text{X-Y}}$. The authors[300] assumed that this model elucidates the mechanism of the Raman effect to a greater extent than the model with $\partial\alpha_{\text{X-Y}}/\partial q_{\text{X-Y}}$ chemical bond increments (see below), in which the "interaction of the dipoles induced in atoms is neglected". In reality neither model (nor the concept of resonance structures[301] and Pauling's oscillations between them[302]) can claim to explain the mechanism of the Raman effect, but the model with bond increments is closer to reality (it reflects, albeit implicity, the involvement of two-centre molecular orbitals and not individual atomic orbitals).

The zeroth approximation of the valence-optical scheme assumes the additivity of the polarisabilities of individual chemical bonds—"independent" molecular fragments. Three increments of α and three increments $\partial\alpha/\partial q$, corresponding to three Cartesian components, one of which coincides with the direction of the bond, are attributed to each bond (for example, C=C, C–Cl, O–H). Strictly speaking these increments have no physical significance even in those cases where their empirical selection leads to satisfactory results for molecules which are most consistent with the additive scheme (saturated hydrocarbons under conditions remote from resonance); in connection with the proof described in an earlier review by the present author[1] (p. 707), one may also refer to new interesting data concerning the splitting of the electronic levels of alkanes[303]. At the same time the possibility of adapting the valence-optical scheme are much wider than in the case of Silberstein's model. However, its use for compounds such as TiI_4, $SnBr_4$, and other coloured compounds[176,197,304] with non-local levels e lacks any justification.

In Lippincott's scheme a purely empirical selection of $\partial\alpha/\partial q$ increments is replaced by a semiempirical calculation[305] but with limitation to a single Cartesian component per bond, which naturally greatly diminishes the possibility of adaptation. The scheme is based on a very primitive one-dimensional model—an electron in a field with two identical infinitely narrow potential wells at the sites of the two atoms forming the chemical bond; here one can imagine an electronic excitation involving a transition between states with symmetric and antisymmetric wave functions; the frequency of the transition naturally diminishes as the bond is extended and the polarisability increases. In conformity with the assumptions made, the derivative of polarisability for $\nu = 0$ in the resulting formula (see, for example, Nagarajan[305] and p. 713 in the earlier review[1]) is proportional to the chemical bond order n. The formula has been used fairly widely for approximate estimates of bond orders from Raman intensities and for converse purposes; for example, a significant degree of π bonding has been noted[243,247,249] in $TiCl_4$ and VCl_4 molecules and in CrO_4^{2-} and MoO_4^{2-} ions. Estimates of bond orders made it possible to refine the force constants[306] for PF_5 and other molecules.

Fontal and Spiro[307] recently proposed a simplified expression for single bonds: $\partial\alpha/\partial q = 0.1\chi q_0^3 n$, where χ is the electronegativity of the atoms and q_0 the equilibrium bond length. On this basis, the authors[307] reached conclusions about the bonds in bridged complexes and about the degree of covalence of certain coordinate bonds.

In the first approximation of the valence-optical (additive) scheme refinements are introduced in the form of additional empirically selected increments attributed to the influence of adjacent chemical bonds and valence angles. With the aid of a standard set of conventional increments (main and additional increments), it is possible to describe the intensities of the Raman lines for various molecules with "weakly interacting" bonds under conditions very remote from resonance. Thus, using 12 parameters of C–H and C–C bonds, determined from the Raman spectrum of cyclohexane, a satisfactory description of the spectrum of polyethylene was achieved[308]. Koenig and Bigorne[309] examined the $Ni(CO)_4$ spectrum and the additive scheme was supplemented by the separate contribution of the lone electron pair of the oxygen atom $\partial\alpha_{lp}/\partial q$.

The use of quantum-chemical LCAO-MO methods to calculate molecular wave functions and frequencies ν_e with subsequent evaluation of α_{01} or $\partial\alpha/\partial Q$ is much more promising and is of greater intellectual value than the computational procedures examined above. Quantum-chemical methods have been used for ethylene, acetylene, and certain other molecules[260,298,299,310], but in most cases only within the framework of the conventional problem of the influence of a static field[311-313].

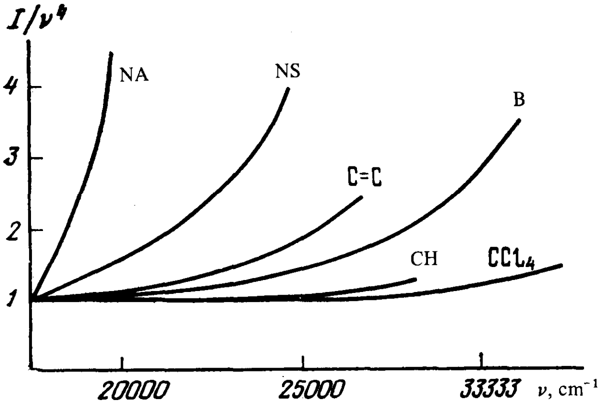


Figure 5. Deviations from proportionality between I_S and ν^4 with increase of the frequency of the exciting light ν and as resonance is approached; the values of the quantities compared are assumed to be unity at $\nu = 18000$ cm^{-1}; NA = p-nitroaniline, Raman line of the nitro-group; NS = p-nitroanisole, Raman line of the nitro-group[145]; (C=C) = line corresponding to the vibrations of the C=C bond in mono-olefins[240]; B = 992 cm^{-1} benzene line[104,314]; CH = 802 cm^{-1} cyclohexane line[314]; CCl_4 = 313 cm^{-1} carbon tetrachloride line[318,319].

VI. THE EXCITATION SPECTRA OF RESONANCE RAMAN LINES

When the spectra of colourless compounds are excited under conditions where the absorption bands are very remote from the incident light frequencies ν, the intensity of all the Raman lines increases smoothly with ν in proportion to the factor $(\nu-\omega)^4$ (see data for cyclohexane[314] and others[315-317]). It followed from the semi-classical theory that, under conditions somewhat less remote from resonance ($\nu_e - \nu < 40000$ cm^{-1}), the intensity may increase much faster owing to the simultaneous increase of α'. This was confirmed by experiments with olefins, ketones, and other compounds with single and conjugated π bonds. These experiments initiated systematic research into excitation spectra, undertaken at one time at the Karpov Physicochemical Institute[10,240]. One of the first results was the demonstration of a large contribution of the modulation of ν_e by the symmetrical vibration of the p-nitroaniline nitro-group on excitation by light corresponding to the long wavelength part of the $\pi \rightarrow \pi^*$ absorption band. Data for several compounds are presented in Fig. 5.

Further studies on p-nitroaniline[145,320,321] yielded an idea about the changes in the intensity coefficient I^S of the line due to the nitro-group over a wide range of frequencies ν [see Fig. 6, where the $\lg I^S(\nu)$ relation is presented; the continuous line corresponds to the direct experiment and its extrapolation, shown as dashed lines, were constructed on the basis of analogies with other data]. With decrease of $\nu_e - \nu$ from 20 000 to 0 cm^{-1}, the intensity I^S increases by a factor of several thousand, in approximate agreement with the contribution of α_e^*; the form of the $I(\nu)$ relation permits an estimate of the decay constant as ~ 2000 cm^{-1}.[322] We may note that, at the frequency corresponding to the same $\pi \rightarrow \pi^*$ absorption band, one may expect only slight changes in the intensity of the C–H Raman lines, which are more closely associated with the $\sigma \rightarrow \sigma^*$ bands in the far ultraviolet.

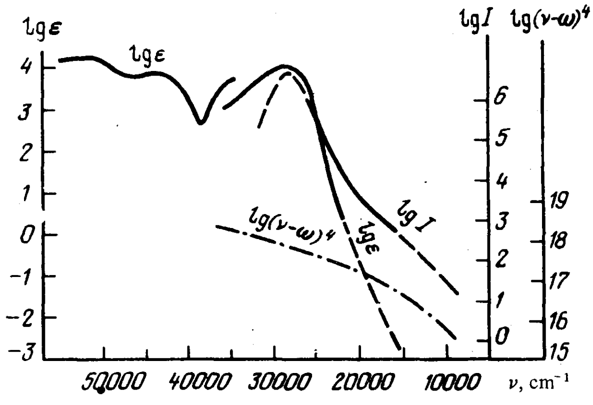


Figure 6. $\lg I(\nu)$ nitro-group line excitation spectrum and absorption spectrum of p-nitroaniline (solutions in benzene)[145,320,321].

The approximate coincidence of the $I(\nu)$ and $\epsilon(\nu)$ maxima was observed not only for p-nitroaniline but also for the majority of other compounds with broad absorption bands; but a deviation by 300–800 cm^{-1} in either direction has been observed for bromine[322,323], solutions of iodine[324,325] and dimethylaminoazobenzene[326], and in many other instances, particularly for overtones[21,142,327].

Bobovich and coworkers[328,329] believe that the $I(\nu)$ maximum must be located in the region of the $00 \rightarrow e0$ transition, i.e. at the beginning of the absorption band [experimental data, see Schmid[5], pp. 284, 340], which is possible, in principle, only in certain special cases—with partial superposition of the bands due to different electronic transitions[324,325,331], when there is marked dependence of γ_{ev} on v, for certain low values of Δ_{em}, etc. The explanation of the causes responsible for the divergence of the $I(\nu)$ and $\epsilon(\nu)$ maxima given by Michaelian et al.[276] is incorrect and has been obtained on the basis of a simple exclusion of the contribution of the short-wavelength part of the absorption band; the interpretation of Friedman et al.[322] does not differ greatly.

An example of a compound with a low decay constant ($\gamma_e < \omega$) and a distinct vibrational structure of the absorption band is provided by the diester EtOOC–(CH=CH)$_6$–COOEt. Fig. 7 illustrates the dependence of $\lg I^S/(\nu - \omega)^4$ on ν for the 1562 cm^{-1} Raman line due to the C=C vibration (the results of a direct experiment are shown by a continuous line); the curve is continued by dashed lines based on analogies with other similar compounds[138,338]. Together with experimental data, the results of calculations are presented for those cases where the intensity is determined by (1) the term b_e in Eqns. (1) of the semiclassical theory (modulation of f_e) and (2) by the formula of the quantum theory taking into account the contributions of individual sublevels ev subject to the assumptions corresponding to $f'_e = 0$ (dashed lines). The values of $\lg I^S/(\nu - \omega)^4$ for $\nu = 5000$ cm^{-1} were assumed to be unity; $\nu_e = 25\,520$ cm^{-1} and $\gamma_e = 250$ cm^{-1}.

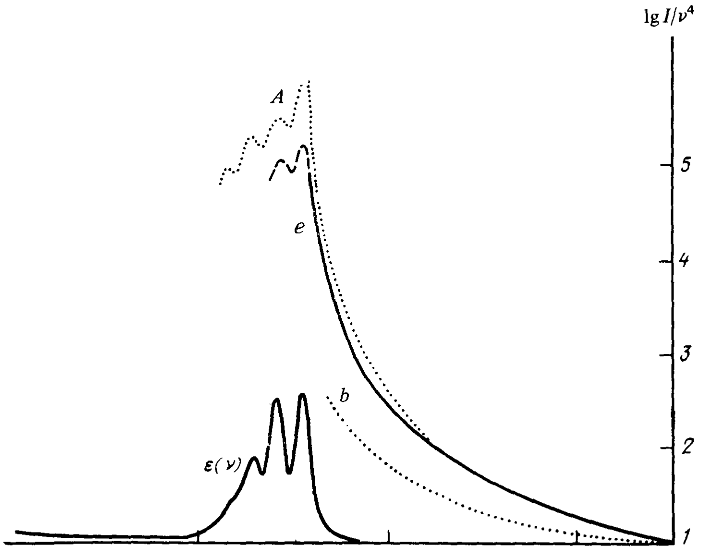


Figure 7. Relative changes in I/ν^4 for the C=C line of the diester (see text) as the region of resonance is approached; e—experimental data; A—calculated data with allowance for the term A_e only; b—ditto with allowance for the term b_e^* (modulation of f_e).

The term a_e^* of the classical theory and the A curve virtually coincide outside the region of resonance and agree with experiment much better than the term b_e and a little better than the term a_e, which shows that the contribution of the modulation of f_e is small. On excitation in the region of the components of the ev fine structure, the semiclassical theory is known to be inapplicable and the A curve, obtained within the framework of the quantum theory, agrees with experiment only qualitatively—it does not reflect the presence of several modes in the ev fine structure. Under conditions remote from resonance, either the contribution of A_e or that of the first absorption band is of secondary importance. We may note that, in the vicinity of resonance, the intensity of the diester line increases much faster than that of the p-nitroaniline line, which is due to the much smaller decay.

During recent years experimental studies have been made on the $I(\nu)$ relation for the Raman lines of many organic and inorganic compounds in the vicinity of resonance[50,243,247,317,329–336] and in the region of resonance corresponding to a structureless absorption band[56,145,148,329] [see also Schmid[5], pp. 328–337, etc.]; in the region of the band with an explicit vibrational structure studies have been made on polyene compounds[147,335–338], metalloporphyrins[202,254,261], haemoglobin derivatives[187], MnO_4^{2-},[168] and others[339–341].

Studies on certain totally symmetric vibrations of diphenylpolyenes[336], nitroaniline[277,321], $TiBr_4$,[342] MnO_4^- ions[159], and other species[160,245,276] led to the conclusion that the modulation of M_e (the term B_e) predominates. The predominance of the modulation of ν_e has been demonstrated for lines due to carotene[335,338], aminoazobenzene[326,343], diethylcyanine[344], haemoproteins on excitation with light corresponding to the Soret absorption band[187,345], nucleotides[99], SnI_4,[275,342] CrO_4^{2-} ions[36], MnO_4^{2-} ions[168], iodine[324,325], and other species[219,246,268,346] in the vicinity or in the region of resonance, as well as benzene[104], butadiene[317], and others[186,347] outside the region of resonance. On excitation with light corresponding to one absorption band, the C=C Raman line of the tetracyanoquinodimethane anion corresponds to the modulation of ν_e and, on excitation with light corresponding to another band, it corresponds to the modulation of M_e.[348] The data for phenazine, pyrazine, and PtI_6^{2-} ions indicate the modulation of ν_e by totally symmetrical vibrations and the modulation of M_e by antisymmetric modes[177,186,349]. According to Schmid et al.,[350] the asymmetric (b_{3g}) vibration line of anthracene corresponds to the frequency multiplier of the term A_e!

Unfortunately the number of experimental points[351,352] on the $I(\nu)$ curves and the information about the electronic absorption spectra and the constants γ_e employed[277,352,353] were in many cases quite inadequate and the set of electronic transitions taken into account was fairly arbitrary[160,241,245,263,276,333,342] and in addition was almost always restricted to the long-wavelength part of the spectrum. Nevertheless a more detailed analysis indicates the great importance of the range 1000–2000 Å[104,316]; thus, according to Ziegler and Albrecht[104], the most effective band for the 992 cm^{-1} Raman line of benzene is much more remote (~ 1200 Å) than the nearest intense absorption band (1830 Å).

Nevertheless, the set of all available data, including the more pronounced $I(\nu)$ relation for overtones[14,139,142] (and for the majority of lines due to 0 → 1 symmetrical vibrations compared with lines due to asymmetric modes[291]), the similarity in the sets of frequencies ω observed in resonance Raman spectra and in the fine structure of absorption bands, as well as the results of certain quantum-chemical calculations[298,299] show that the term A_e predominates in the vicinity of resonance for the majority of lines due to totally symmetrical vibrations.

As an example, we may mention the results of calculations of the intensity and scattering activity (which does not include the multiplier ν^4)[1,7,15], obtained[298] by the CNDO/C method for the Raman lines of ethylene in all three versions, which demonstrate the relative contributions of M'_e and ν'_e under conditions remote from and close to resonance (Table 2); Table 3 provides information about the contributions of the factor ν'_e for the six most important levels e, the first of which corresponds to the excitation of π electrons and the remainder correspond mainly to the excitation of σ electrons[298].

Calculation of the intensity of the C=O line of benzaldehyde[310] under conditions remote from resonance indicates the predominance of the factor M'_e for the majority of the levels e.

Table 2. Calculation of the scattering activities for the C-H (3019 cm^{-1}) and C=C (1623 cm^{-1}) ethylene lines.

ν, cm^{-1}	C–H			C=C		
	calc. with allowance for different factors			calc. with allowance for different factors		
	M'_e	ν'_e	M'_e and ν'_e	M'_e	ν'_e	M'_e and ν'_e
8 000	67	3	93	8	6	14
16 000	77	4	107	8	19	27
24 000	132	5	152	9	520	510

Table 3. Calculation of $\nu'_e M^2_e$ for the C-H and C=C ethylene lines.

ν_e, eV	$\nu'_e M^2_e$		ν_e, eV	$\nu'_e M^2_e$	
	C–H	C=C		C–H	C=C
6.41	0.4	−5.6	13.40	−1.6	−1.2
8.93	−2.4	−1.6	15.75	−13.6	1.6
12.50	−1.6	0.4	16.13	−1.2	−0.4

The excitation spectra of the Raman lines resemble electronic absorption spectra (see the examples quoted in the literature[24,254,329,340]), but for many complex molecules the $I(\nu)$ bands are much narrower and the excitation spectrum reveals the concealed structure of the broad absorption band formed as a result of the superposition of many components (Fig. 8).

Summarising, the following may be said. The positions of the Raman lines in resonance Raman spectra characterise the ground electronic state of the molecule; the excitation spectra of resonance Raman lines provide information about electronically excited states, which frequently cannot be secured by measuring the absorption spectrum.

The excitation spectra have been used to solve a very wide variety of problems underlying in one way or another more advanced stages associated with the study of molecular structures and chemical transformations: 1. The elucidation of the mechanism of the Raman effect (the type of modulation, the contribution of the Frölich interaction in semiconductors[22,82] etc.), and test of the validity of particular variants of the theory. 2. The separation of resonance Raman and fluorescence lines. 3. The determination of the role of various absorption bands and of their contributions to the intensities of specific Raman lines[99,317,334,354]. 4. The determination of the concealed structures of absorption bands (see Section VII). 5. The elucidation of the type, location, symmetry, and energy of electronic excitation[156,184,187,340,346,355,356]. 6. The determination of the width of the forbidden gap in the components of binary semiconductor compounds. 7. The derivation of information about the geometry of the molecule and the frequencies ω in electronically excited states[100,103,257,258,334]. 8. The estimation of the lifetime of the excited state τ_e in the case of a non-uniform broadening of the adsorption band[290] (which cannot be done on the basis of the absorption spectrum). 9. The construction of the $E_e(Q)$ potential energy curve when bands due to different electronic transitions are superimposed[289]. Other applications of the excitation spectra as well as individual examples will be given in the next section.

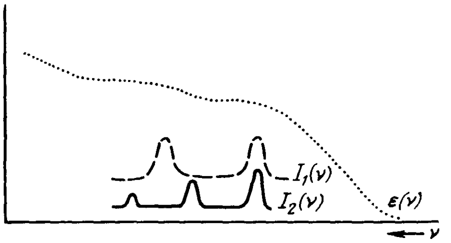


Figure 8. Excitation spectra of two Raman lines (ω_1 and ω_2) of a hypothetical complex molecule.

There is no doubt that the joint investigation of absorption and resonance Raman excitation spectra is extremely useful and improves the effectiveness of spectrochemical studies.

VII. CHEMICAL APPLICATIONS OF RESONANCE RAMAN SPECTROSCOPY

The applications of resonance Raman spectroscopy are based on determinations of the frequencies ω, the molar intensities I, the degrees of depolarisation ρ, and $I(\nu)$ line excitation spectra. The experimental data are used on the basis of theoretical generalisations and empirical relations which determine the relations between the parameters of the spectra and molecular structure.

The ways in which the information about the Raman and resonance Raman line frequencies is used are in principle the same; the most important trend in this field involves the detection of specific structural groups in the molecule and the determination of their positions as well as the characterisation of the state and rigidity of the chemical bonds. However, resonance Raman spectra give rise to the following additional possibilities: 1. An extension of the set of frequencies ω susceptible to measurement as a result of the discovery of lines forbidden by the usual selection rules (for example, inversely polarised lines). 2. The detection, identification, and investigation of the structures and chemical transformations of trace impurities[357], biologically active compounds present in very low amounts, impurity centres in crystals, etc. 3. The study of the structure of short-lived intermediates. 4. The characterisation of monomeric products in the absence of association at very low concentrations (10^{-4}–10^{-8} M[326,337]). 5. The determination of the frequencies of overtones (and the components of their isotopic structure) and of the coefficients of the anharmonicity of the interatomic potentials with the corresponding revision of the molecular force field, dissociation energy, etc. 6. The isolation of the frequencies ω and characterisation of specific chromophoric groups in complex molecules. According to Baierl et al.,[68] the moments of inertia and centrifugal deformation constants may be determined from rotational resonance Raman spectra no less accurately than from electronic absorption spectra.

The available information about the line intensity makes it possible, in principle, (1) to characterise the change in the polarisability of molecules on extension of specific chemical bonds and, on this basis, the bond order, (2) to investigate the kinetics of the reactions of unstable species and intermediates, (3) to determine quantitatively the content of microimpurities, the distribution of molecules with respect to orientation[28,61], the distribution of inhomogeneities on the surface of a solid under static conditions and in the course of chemical reactions, as well as equilibrium constants at low concentrations, (4) to demonstrate the involvement of particular atomic groups in conjugation and in the given type of electronic excitation, (5) to determine the location of the active centre responsible for the formation of an intermediate complex or the transition state, and (6) to determine, when the assignment of the resonance Raman lines is known, the type and location of electronic excitation (and conversely)[143,340,352,358].

We shall now consider in greater detail individual aspects and specific examples. In very complex molecules containing thousands of atoms the number of normal atomic vibrations is extremely large. The detection and assignment of individual lines and the derivation of useful information from the spectrum excited under conditions remote from resonance are difficult or impossible. However, when the Raman spectrum is excited in the region of the absorption band of a specific chromophoric centre, a very limited set of frequencies ω for the centre, susceptible to interpretation, is isolated. Thus, when the resonance Raman spectrum is excited with light corresponding to the long-wavelength absorption band of haemoproteins, it is possible to observe the intense lines due to the metalloporphyrin system without any interference by the protein fragments which incorporate more than 99% of the total number of atoms of the metalloprotein. The same situation arises on excitation of the lines due to the thiouracil residue of modified RNA.[98] If the molecule contains several different unconnected chromophoric centres, it is possible to excite the resonance Raman spectra of each independently. By varying the frequency of the exciting light, it has been possible to isolate consecutively the resonance spectra of systems with different numbers of conjugated double and triple bonds in polymers; thus the statistics of the distribution of conjugated systems has been characterised[359] in terms of the number of π bonds in such systems and data have been obtained on their structures and transformations as the temperature is altered.

A high intensity of the low-frequency lines due to the vibrations of bonds with a heavy atom has been noted for many compounds, the intensity increasing further on excitation with light corresponding to absorption bands associated with charge transfer along the bond[184,355,360,361]; an example is provided by the Ni–C line in the $Ni(CO)_4$ spectrum[309]. The intensification frequently extends to the lines for the atomic groups of the ligand adjoining the heavy atom. These factors have been used to assign the Raman lines (or the absorption bands corresponding to the wavelength used to excite the resonance Raman effect) and in structural studies[143,156,362,363]. Thus the enhanced intensity of the lines due to the phenolic group of tyrosine in the resonance Raman spectrum of Fe-transferrin[364] and their normal intensity for stellacyanin[365] served as a basis for inferring the structure of the region of active centres in these metalloproteins; the spectrum of stellacyanin indicates a quasi-tetrahedral coordination of copper with participation of nitrogen atoms, which can be inferred from the intensification of lines due to the amide group.

A study of the resonance Raman spectra of $NaClO_3$ crystals irradiated by a beam from an electron accelerator revealed the formation of two types of unstable ClO_3 radicals differing in their positions in the crystal lattice and in the kinetics of their decomposition; the excitation spectra showed that definite (different) regions of the ~ 5500 Å broad absorption band correspond to these types; the authors[38,39] note that, without an appreciable resonance intensification, the observation of the Raman lines would have been impossible owing to the rapid decomposition and low concentration of the radicals.

The resonance Raman lines of impurity centres (O_3^- ions) formed in chlorates on γ-irradiation have a multiplet structure and the excitation spectra of individual components of the multiplets are different. The results indicated the formation of four types of ion with different orientations; they made it possible to estimate their distribution with respect to orientations, to derive information about the mechanism of the radiolysis, and to demonstrate the formation in the first stage of ClO_3^{2-} ions, which decompose by several paths[40]. The formation of metastable O_2 molecules with a slightly reduced bond rigidity on radiolysis has been demonstrated by the same method[38,39].

The study of excitation spectra has shown that the intensity of the C=C lines of alkenes and dienes is determined mainly by the $\pi \rightarrow \pi^*$ long-wavelength absorption band (~ 1800 Å and correspondingly ~ 2200 Å[240,317]), the changes in interatomic distances in the $\pi \rightarrow \pi^*$ transition being rather significant and corresponding to $\Delta_{C=C} = 0.08$ Å and $\Delta_{C-C} = -0.055$ Å in the case of tetrachlorobutadiene[103].

The separation of the contours of broad absorption regions into zones corresponding to different vibro-electronic transitions on the basis of resonance Raman excitation spectra has frequently proved very effective[142,366,367]. Thus it has been possible to observe weak components, which are virtually indistinguishable on the basis of $\epsilon(\nu)$ curves, for example the long-wavelength electronic transition in polyenes[368-370], to detect in the broad contour of an absorption band several electronic transitions in those cases where only one had been postulated[215,355], to determine the frequency of the purely electronic $00 \rightarrow e0$ transition and other ev components[215,340,371,372] [thus a single C≡N line gave rise to seven $I(\nu)$ maxima at the wavelength corresponding to the absorption band of tetracyanoquinodimethane radical-anions, the maxima being assigned to elements of the vibrational structure[366]], to isolate absorption regions referring to very similar compounds present simultaneously in a complex product (for example to different haemoproteins, to conjugated systems of different lengths in polymers and to incompletely equivalent impurity centres in crystals) and to characterise further their structure, to determine the structure of the conductivity band of crystals which is difficult to investigate[24,35,85], and to determine the location of the lines due to dipole-forbidden exciton transitions in the absorption spectrum[285].

Thus measurements of excitation spectra assist in a more complete interpretation of the absorption spectra and hence extend the scope of structural analysis.

An exceptionally high sensitivity of the intensity to conjugation conditions has been noted also outside the region of resonance in a number of studies. Certain molecules (and ions) hardly differ as regards the frequencies ω and ultraviolet absorption spectra but have very different resonance Raman line intensities; examples are provided by tetracene[373] and triphenylmethane (Schmid[5], p. 300) anions and cations. When complexes with weak bonds are formed, the frequencies ω of the components hardly change, while I^S may increase by several orders of magnitude (complexes of tetracyanoethylene with aromatic hydrocarbons[374], etc.). A sharp increase of the Raman line intensities has been described for certain colourless compounds in contact with molecules of dyes[94 6] and with a metal[375,376], which is probably due to the breakdown of the localisation of electronic excitation.

Moschalski and Schmid (see Schmid[5], p. 46) showed, using excitation in the visible part of the spectrum, that the stretching vibration line due to the two non-conjugated C=C bonds in norbornadiene has a reduced intensity owing to the interaction of the π bonds through space; with increase of the distance between two C=C bonds in other hydrocarbons, the line intensity approaches the normal value. Evidence for conjugation has been noted in the spectra of cyanoepoxyethane[377] and π-electron systems linked by -NH- and -S- bridges (Ph-C=C-S-C=C-Ph, etc.[378]) and has been studied in detail for a large number of PhX molecules. The data obtained for the intensity of the polarised line of the benzene ring at ~ 1600 cm^{-1} have been used to determine the angle of rotation of the plane of the benzene ring in the presence of steric hindrance[336,379] and to investigate the relations with Hammett and Taft constants[1,420]. The contributions of n,π-conjugation in such systems are considered by Epshtein et al.[380] to be fairly small and masked by the influence of certain differences between the vibration modes.

The determination of resonance Raman line frequencies has been used to solve a very wide range of problems. For example, it made it possible to estimate the degree of charge transfer and the charge distribution in certain donor–acceptor complexes[381] and ions[382], having resolved controversial questions concerning their structure, to determine the rigidity of the bonds between F-centres and crystal lattice atoms[43], to establish an appreciable double bond character of the C–N linkage in the p-phenylenediamine radical-cations[30], to discover a significant redistribution of electron density from phenyl groups to the main chain in polyphenylacetylene[25], to obtain new data on the structures of iodine–amylose complexes, indicating the presence of chains comprising ~ 28 iodine atoms in which it is possible to distinguish three-atom units[383], to show that the impurity centres in natural pale-yellow fluorite crystals are O_3^- ions[37], to determine the differences between the valence states of two ruthenium atoms in a pyrazine complex[356], etc.

The mechanism of the reactions of diphenylethylene following its adsorption on silica gel has been studied recently; the appearance of new resonance Raman lines in the first stage was attributed to the formation of a carbonium ion, which is rapidly converted into a π-complex, the spectrum being modified further (see Schmid[5], p. 298).

According to certain data[384,385], it is possible to distinguish and characterise azo-quinonoid and intermediate forms of acid–base indicators (aromatic azo-compounds) and to refine ideas about the mechanisms of their reactions at varying pH and low concentrations, which correspond to the conditions under which they are applied in practice. According to Machida et al.,[384] when alkaline solutions of Methyl Orange are acidified, the azo-group is protonated and the indicator is converted into acid forms close to a quinonoid type; on the other hand, the azo-forms of analogous hydroxyphenylazo-compounds persist. The formation of Methyl Orange complexes with serum albumin modifies the colour changes of the indicator; however, the study of the spectrum disproves the conclusion that the azo-form undergoes a *trans* → *cis* transition and that a proton is transferred from the protein[386].

The resonance Raman spectra of Tropaeolin O reflect three stages in its colour changes and consecutive protonation as the pH is reduced. Saito et al.[385] determined the equilibrium position under conditions corresponding to the simultaneous presence of several forms (whose total number is 8) at all the stages of the colour changes and characterised the state of the π-electron system in each form. According to the results, the triply charged anions (judging from the spectrum, they resemble an azo-structure but with appreciable delocalisation of excess electron density) are converted into dianions, which may be present in three forms, including the quinonoid form, then into monoanions (quinonoid and azo-forms), and finally into neutral molecules which are said to exist[385] in a zwitterionic "hybrid" form similar to the quinonoid form.

The appearance of the intense 160 cm^{-1} line in the spectrum of the dimeric cations of p-phenylenediamine on excitation with light corresponding to the charge-transfer absorption band served as the basis for assigning this line to the intermolecular vibration in the dimer and for the corresponding estimate of the force constant of the bond between the dimer components (0.82×10^5 dyn cm^{-1})[387].

An exact determination of the frequencies of the overtones has been used to find the dissociation energy of I_2^- ions in a matrix (20 kcal $mole^{-1}$),[178] the heat of atomisation of O_3^- ions (153 kcal $mole^{-1}$), the electron affinity of ozone molecules (42 kcal $mole^{-1}$),[44] etc.[184]

Resonance Raman spectra are widely used to investigate metalloporphyrins and, in the words of Yamamoto et al.[388] "constitute a highly effective means for the investigation of haemoproteins". Experiments have shown that when the resonance Raman effect is excited by light corresponding to the $\pi \rightarrow \pi_1^*$ absorption band (~ 5000 Å), the lines of a number of non-totally symmetric vibrations with participation of the C–C and C–N bonds of the macroring are particularly strongly intensified; on excitation with light corresponding to the Soret band (~ 4000 Å), mainly the lines of the fully symmetrical modes, including low-frequency modes with participation of bonds involving the metal atom, are preferentially intensified[255]. Certain characteristic resonance Raman lines have been used successfully as spin indicators and indicators of the state of oxidation of the metal atom[129,360,389], of the breakdown of coplanarity of the metalloporphyrin system[188], and of the change in the quaternary structure of a protein[207]. The positions of these lines in the spectrum are associated with the conjugation conditions and the rigidity of the π bonds in the macroring[218,339,390].

We shall now present several examples. The study of the frequencies of the indicator lines led Kitagawa et al.[391] to the conclusion that there are two types of low-spin ferrohaemoproteins differing in the type of bond with the fixed (axial) ligand: with coordination of the lone electron pair of the ligand atom to the unfilled d_{z^2} orbital of the Fe atom (cytochromes) and with $d_\pi(\mathrm{Fe})-\pi^*(\mathrm{Lig})$ interaction (oxyhaemoglobin, myoglobin, nitrosohaemoglobin). The indicator line for the interaction with ligands indicates the replacement in stages of the sixth ligand in the haem groups in ferrocytochrome c_3 as the pH is raised[392]. In certain high-spin ferri-haemoproteins (chloroperoxidases) the frequencies of the indicator lines are reduced, which indicates a shift of electron density from the axial ligands to the porphyrin system accompanied by population of the anti-bonding π^* orbital and the corresponding decrease of the rigidity of the π bonds[393]. Indicators of the breakdown of coplanarity (reflecting the conjugation conditions in the metal–porphyrin system[218]) demonstrate, according to Felton et al.,[206] the displacement of the Fe atom from the plane of the four nitrogen atoms in oxidised hydroperoxidases by ~ 0.5 Å; indicators of the spin state disprove the conclusion that there is an equilibrium between states with 5/2 and 3/2 spins.

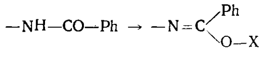
The presence of the characteristic intense 1373 cm^{-1} line confirms that protohaemin incorporates Fe^{3+} ions; the ~ 1500 cm^{-1} line is characteristic of a high-spin state of iron and of a non-planar structure of the chromophore, but in the complex with imidazole it is located in a higher position and indicates a low-spin state and a planar structure for the same oxidation state of iron[345].

The study of anomalous forms of haemoglobin[394] showed that the position of the Fe atom relative to the plane of the haem group in α-chains is not altered when iron in the β-chain is reduced and thus the quaternary T-structure is retained.

The possibility of recording the changes in the resonance Raman spectra of haemoglobin as the partial pressure of oxygen is altered has been noted[53]. It is suggested that the resonance Raman effect may serve as the basis of apparatus for clinical studies on blood (see Schmid[5], p. 212).

The study of the resonance Raman spectra of oxyhaemerythrin—an oxygen transferring agent of a non-haem type—made it possible to exclude structures with equivalent oxygen atoms from the five proposed versions of the structure; in azidomethaemerythrin all three nitrogen atoms are located in non-equivalent positions[395]. Eight models of oxyhaemocyanine, an oxygen-carrying metalloprotein from the haemolymph of molluscs, have been considered in the literature. The frequencies of the resonance Raman lines correspond to a non-planar structure in which the bound oxygen exists in the form of a peroxide ion and the copper atoms are present in the bivalent state[396–398].

Carey and Schneider[399] noted that resonance Raman spectroscopy is a very useful instrument for the investigation of the mechanisms of enzymatic catalytic reactions and may yield extensive information about the modifications of individual atomic groups on formation of intermediates when enzymes interact with coloured substrates; furthermore, the deformation of the substrate is one of the factors responsible for the increased rate of reaction. According to the authors, the intermediate formed in the reaction of papain with an ester containing the α-benzamide group has a sharply different resonance Raman spectrum compared with the initial and final products[400,401]. The spectrum indicates changes in the acetyl group and a rearrangement of the benzamide group of the substrate:



$$-NH-CO-Ph \rightarrow -N{=}C\begin{matrix}\diagup Ph \\ \diagdown O-X\end{matrix}.$$

New data on the structure of enzyme–inhibitor complexes have been obtained in a number of studies[402–404]. For example, it has been shown that the sulphonamide group in certain derivatives of sulphonamidoazobenzene in complexes with carbonic anhydrase B is ionised and that the coplanarity of the azobenzene group is significantly distorted.

Resonance Raman spectroscopy has been used to determine the types and locations of enzyme modifications. It has been established that, when carboxypeptidase reacts with arsanilic acid, the tyrosine-248 group is modified; the reaction of carboanhydrase with diazobenzenesulphonamide results in the diazotisation of the histidine residue (see Schmid[5], p. 206).

Carey et al.[406] investigated the applications of resonance Raman spectroscopy in immunochemistry, particularly for the determination of the active centres of antibodies and the structure of complexes with haptens. The resonance Raman spectra of such complexes reflect the perturbations induced by the interaction with the protein, including the changes in the state of ionisation and conformation of individual fragments. The authors investigated the lines of bound coloured haptens (dinitrophenylazonaphthalenedisulphonic acids), characterised the changes in conformation, and demonstrated a decrease of the amount of double bond character in the N–O linkage in both nitro-groups as a result of the influence of the specific charge distribution in a particular fragment of the antibody. The studies established the changes in conformation favouring contact with the active centres of antibodies isolated from mouse tumours.

Resonance scattering has been used to detect traces (⩾ 0.0001%) of polyene compounds in thermally degraded specimens of poly(vinyl chloride). On excitation of the spectrum at different frequencies, systems with different numbers of units were excited. Thus an increase of the average chain length of conjugated C=C bonds with increase of temperature and of the duration of heat treatment of the polymer has been demonstrated[357].

The spectra of the carapaces of live crayfish demonstrated the presence of astaxanthin bound to a protein[405]. Distinct lines of carotenoids were detected in the resonance Raman spectrum of the sciatic nerve of the frog[407]. The presence of β-carotene, bound in the membranes of erythrocytes (predominantly in cholesterol-depleted regions) has been demonstrated[408] and its content determined (7×10^{-4}% relative to the weight of lipids); the increase of the intensity of the characteristic lines when the membrane is acted upon by trypsin and lysolecithin is regarded as an indication of the modification of the carotene molecules as a result of the decrease of the internal strain in the surrounding regions; sharp changes in intensity with increase of temperature above 17°C indicate changes in conformation (see Schmid[5], p. 178).

In Lewis's words, resonance spectroscopy is exceptionally effective in the study of visual processes. With the aid of resonance Raman spectroscopy, Lewis investigated the transformation of rhodopsin at different stages of the dark adaptation of a functioning eye[54,414]. New data have been obtained[118,409] for the structures of intermediate products in very rapid multistage transformations of bacteriorhodopsin—a photosynthetic system which ensures proton transfer via cell membranes of halophilic bacteria. Other examples in the field of biochemistry have also been described[401,410–420].

Resonance Raman spectroscopy has been used successfully to study the mechanisms and kinetics of electrochemical processes. The advantages of the method compared with infrared spectroscopy (higher sensitivity and the possibility of employing aqueous solutions and metallic electrodes), ultraviolet spectroscopy (a greater yield of information), and EPR (the possibility of studying ions, neutral molecules, and radical-ions) have been noted[62]; the method is suitable for the investigation of organic, inorganic, and organometallic electrosynthesis[63].

The ways of using resonance Raman spectroscopy to probe the atmosphere and to determine the substances contaminating air at heights up to 10 km (Raman radars), to determine from a flying aeroplane the presence of certain coloured components in air over the surface of the sea in order to estimate its bioproductivity[421–423], etc. are being investigated. The possibility of using resonance Raman spectroscopy in the study of the atmospheres of other planets is not ruled out.

CONCLUSION

In recent years a major contribution has been made to the development of the spectroscopy of resonance light scattering by molecules and crystals. The improvement of the experimental techniques and theories and the study of correlations between the spectra and the structure of molecules and their physicochemical properties greatly extended the basis for a wide variety of applications of resonance Raman spectroscopy. According to the authors of a number of studies, "resonance Raman spectroscopy has become a powerful method for the investigation" of molecular structures[253], elementary excitations of the crystal lattice[35,424], biochemical processes[346], electronically excited molecular states[425], vibronic interaction[426] of polymers and oligomers with conjugated bonds[25], and haemoproteins[388] and has become "a powerful analytical tool"[331,337]. The method combines the high sensitivity characteristic of ultraviolet spectroscopy with the high resolution characteristic of microwave and infrared spectroscopy[28,62]; as regards the amount of information which can be derived, the method can be, in principle, superior to infrared and ultraviolet spectroscopy taken together. Despite the number of limitations of the method, many new useful data have been obtained with its aid in chemistry, physics, and spectrochemistry. The use of a more advanced technique (among others, for the measurement of the Raman line excitation spectra and for the investigation of the phenomenon by time scanning[9,117,427,428]) will promote the development of new productive research fields.

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Linear Free Energy Relations as a Means of Generalising and Analysing Extraction Data

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Data concerning the principal ways of "condensing" information about extraction equilibria are surveyed. It is shown that, together with the Law of Mass Action, equations based on linear free energy relations constitute an important means of generalising and analysing extraction data. The linear equations reviewed make it possible to describe quantitatively in an abbreviated form the influence of the structure of extractants, the nature of diluents, the nature of the anionic ligands and the cations extracted, and the phase composition on the extraction equilibria in a series of extraction systems, with the aid of relations between the extraction constants and the parameters σ, E_s, ID, H, IE, and IAP, characterising the influence of the factors indicated. Certain general characteristics of the influence of these factors on extraction equilibria and on selectivity, found with the aid of the linear correlations, are described.

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I. INTRODUCTION

During the last decades, there has been a collosal growth of information about extraction problems, which still continues. Altogether about 10 000 papers have been published[1] and in the last five years the number of annual publications has doubled[2]; at the present time not less than a thousand papers are published annually[3]. A simple list of systems for which extraction equilibria have been studied occupies hundreds of pages[1,4,5]. At the same time, despite the advances achieved in the elucidation of the general characteristics of extraction and the generalisations made, whereby many properties of extraction systems can be explained and predicted qualitatively, an adequate systematic arrangement of the available experimental data has still not been achieved.

One of the important procedures facilitating the use of the extensive information about extraction involves the publication of handbooks[6-8], and monographs with reference data[4,5]. However, the cumbersome nature of reference data involving a direct description of all the values of the partition coefficients for various systems under different conditions limits the scope of the publication of sufficiently complete handbooks of acceptable size. This makes it necessary to "condense" extraction data, i.e. to transform the accumulated information on the basis of general relations which have been discovered (particularly during the last decade). Sukhotin[9] pointed out that, as a result of the condensation of information, partial information derivable from more general information need no longer be retained in memory and can be abbreviated; at the same time the number of symbolic means used for the fixation of information is reduced without impairing the amount of information.

The aim of the present review is to consider the main results of studies devoted to the condensation and analysis of information in the field of extraction (particularly extraction equilibria) and to attempt an assessment of the possible ways towards this end, particularly the use of linear free energy relations for the further development of studies in this field.

II. THE USE OF THE LAW OF MASS ACTION AND CALCULATION OF EXTRACTION CONSTANTS—THE FIRST STAGE IN THE "CONDENSATION" AND ANALYSIS OF INFORMATION ABOUT EXTRACTION EQUILIBRIA

The most significant step towards the condensation of information in the field of extraction was made for the first time, approximately twenty years ago, by Fomin and his coworkers[10-13], who laid the foundations of a new field—the mathematical description of extraction processes based on the consideration of the latter as chemical reactions obeying the Law of Mass Action (LMA). The creation of a mathematical model of partition based on LMA makes it possible, in principle, to replace the set of partition coefficient data for each given series of the type extraction–diluent–aqueous acid (or salt) solution–compound of the extracted element at different concentrations of the components by a single quantity—the extraction constant combined with the equation of the mathematical model.

The simplest mathematical models, which are of great practical importance, but are applicable to a limited range of concentrations, have been devised in numerous fundamental studies[10-13] on the basis of LMA in the concentration form. The mathematical description of extraction equilibria on the basis of LMA made it possible to (1) determine the stoichiometry of extraction reactions by analysing the dependence of the partition coefficients on the quantitative phase composition (the "dilution" method based on equations which follow from LMA) and (2) to obtain information about complex formation, association, changes in activity coefficients, and other phenomena in solutions by analysing deviations from the distribution predicted by LMA. Numerous deviations from LMA did not lead to the abandonment of this law for the description of extraction equilibria and are regarded as a result of the influence of certain interactions in the system on the ideal distribution.

Since LMA in the concentration form does not in general hold over a wide range of concentrations (owing to failure to take into account complex formation by the components and the discrepancies between their activities and concentrations), the models derived from this form of LMA may also not hold. This made it necessary to develop models applicable over a wide range of concentrations, which take into account complex formation and deviations of the activities of components from their concentrations

The region of applicability of models is expanded in two ways: (a) by introducing into the relevant formulae, which include the thermodynamic extraction constant (independent of the concentrations of the components), the activity coefficient† of each system component and coefficients characterising the degree of binding of the components in complexes[11] or (b) the use of "apparent extraction constants" (these values are calculated from empirical equations fitted to the dependence of the constant on the ionic strength of the solution), which vary with the solution composition, without introducing the above coefficients.

The development of the first procedure depends on the development of the theory of solutions, since it requires the development of methods for the prediction and theoretical calculation of the activity coefficient of the components in relatively concentrated solutions of electrolytes. Certain advances have been made in the solution of this problem[14-16], but much work still needs to be done before the solution is sufficiently completely solved. In order to develop the second procedure, it is merely necessary to accumulate experimental data on partition over a wide range of concentrations of the components and to derive empirical equations which agree most precisely with the experimental data. Studies of this type include those[18-21] with a largely practical aim (to calculate the countercurrent distribution). Thermodynamic or at least effective constants, calculated within the framework of the first approach, would evidently be more suitable for generalisations in the chemistry of extraction equilibria.

The cumbersome nature of the computational formulae required for the determination of the activity coefficients of the components[14-16], and also the difficulty of fitting equations to the experimental data to find the "apparent extraction constants", for a long time prevented a large-scale application of these methods. For this reason, the mathematical models based on LMA have so far been designed for a relatively small number of extraction systems among those which have been investigated—for the simplest systems or systems with the greatest practical importance; extraction constants have been calculated only for several hundred systems. However, in recent years it became possible to develop mathematical models on a wider scale and to "condense" partition coefficient data to the level of extraction constant data, as a result of the employment of computers. The latter make it possible to carry out routine calculations on extraction equilibria (even on the basis of extremely cumbersome formulae), such calculations being rapid and requiring little effort[22,23].

It may be expected that improvement of mathematical partition models and the development and large-scale employment of the corresponding computer programs will lead to a more systematic "condensation" of partition data at different concentrations of the components and to their transformation into a single quantity (the extraction constant) for each series of systems of components of the same type. This tendency has been confirmed by the publication in 1974 of a handbook[24] on extraction equilibrium constants.

During the last decade, much work has been done on the higher stages in the hierarchy of studies directed towards the condensation of information in the field of extraction. Factors influencing the extraction constants when not only the concentration but also the nature of the system components is varied have been surveyed. Mathematical models describing sets of extraction constants for different series of systems, differing in the nature of the components, have been created; these models involve a smaller number of constants—parameters characterising only the nature of the components. Whereas in the first stage of the above hierarchy the LMA served as the basis for generalisations, in the next stages equations based on linear free energy relations (LFE) are most frequently used[25]. Generalisations became possible in higher stages despite the imperfection of the development of the first stage, since in many instances (when only one component is partitioned) the partition coefficients of the elements D, measured within the limits of a given series for identical quantitative phase compositions, are proportional to the extraction constants K, which permits a comparison of the values of D instead of K. Equations based on LFE have already been used for a long time in theoretical organic chemistry[26,27], whence they have been transferred to extraction chemistry.

III. LINEAR FREE ENERGY RELATIONS (LFE) AS A MEANS FOR FURTHER GENERALISATION OF EXTRACTION CONSTANT DATA

1. Earlier Applications of LFE in Chemistry

An equation based on the LFE principle was widely used for the first time in 1940 by Hammett[28] to generalise data concerning the influence of the structure of organic compounds on equilibrium constants and rates of various reactions. Hammett established that the following relation is valid for a series of different organic reactions:

$$\lg K = \lg K_0 + \rho \Sigma \sigma, \tag{1}$$

where K are equilibrium constants or rates of reactions of the same type (with a single reaction centre within the limits of the series) for different substituents in the benzene ring, σ are parameters characterising the influence of the nature of the given substituent and independent of the type of reaction series, and K_0 and ρ are quantities independent of the type of substituent and constant for the given reaction series. The quantity ρ is sometimes called[26] the sensitivity coefficient, since it shows to what extent K varies within the limits of the series under the influence of changes in σ.

A scale of parameters σ^* for substituents attached directly to the reaction centre, a scale of parameters σ_P (for substituents attached to a phosphorus atom)[30], and certain other scales for various types of inductive effects

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† In certain cases the activity coefficients are determined experimentally[17] from extraction data.

were proposed subsequently together with the scale of parameters σ, characterising the influence of substituents on the reaction centre attached via the benzene ring. Together with the σ scales, characterising the electronic effects of substituents, scales of the parameters E_S and E_N, characterising steric effects, were also put forward[31–33].

Later equations of type (1) found applications in the quantitative description of the influence on organic reactions not only of the structure of the compounds but also of a number of other factors. Several parameters (for example E_T), characterising the influence of the nature of the solvent, were proposed[26] (equations of the type $\lg K = \lg K_0 + aE_T$). The influence of the nature of the outgoing group was estimated with the aid of nucleophilicity parameters H and equations of the type $\lg K = \lg K_0 + bH$, etc. A detailed survey of the applications of LFE in organic chemistry is given in two monographs[26,30].

Relations based on LFE have been found during the last decade also in inorganic chemistry. Thus linear correlations have been discovered between the logarithms of acid dissociation constants and the logarithms of the stability constants of the complexes formed by their anions with metal cations[34,35–41].

In essence LFE also serve as the basis of a method of comparative calculation of the physicochemical properties of inorganic compounds, which has been used in a number of studies[42–44].

2. The Application of LFE in Extraction

Since 1964–1965 the wide-scale applicability of equations of type (1) in the description and analysis of relations in organic chemistry has attracted the attention of investigators in the field of extraction. Attempts were made to extend the application of LFE to the quantitative description of the influence of various factors on extraction equilibrium constants[25,45].

The influence of the structure of the extractant. In the first place it was suggested that LFE be used to predict the extraction capacity of nucleophilic extractants, i.e. extractants (S :) which form an extractable complex with the electrophilic compound to be extracted (A)—an acid or a metal salt—as a result of a donor–acceptor interaction of the type $S\overrightarrow{:}A$.[46,47] Evidently the stability of the extracted compounds of the type $S\overrightarrow{:}A$ and the corresponding extraction constants (when the extractant is sufficiently hydrophobic) must be higher the higher the mobility of the electron pair in the functional group of the extractant molecule, i.e. the higher the basicity of the latter. For a series of extractants with the same functional group, for example, phosphate esters $(RO)_3PO$, one may expect an increase of extraction capacity with increase of the positive inductive effects of the substituents R and with decrease of the steric hindrance by these substituents in the formation of compounds of the type $(RO)_3PO\overrightarrow{:}A$. It is therefore natural to suppose that the constants for the extraction of a given substance A by a series of extractants with variable substituents and a constant functional group should be related by equations of type (1) to parameters characterising the inductive or steric effects of the substituents. This hypothesis was put forward for the first time in 1964–1965, independently in a number of studies[48–51], in relation to organophosphorus extractants and to extraction by amines[46]. They were tested experimentally initially for series of extractants where changes in substituents differing in inductive effects did not lead to significant changes in the steric hindrance in the interaction of the extractant with the compound extracted. In certain cases series were selected in which the expected changes in inductive effects would be very large and would greatly exceed the possible influence of steric effects. A satisfactory validity of the linear relations between the logarithms of extraction constants and the values of Σσ for the substituents was obtained for such series. Table 1 presents the σ parameters of the substituents used for the correlations and Table 2 lists the correlations found for the equilibrium constants of extraction reactions leading to the formation of the following extractable compounds (here and henceforth the equilibrium constants for reactions involving the formation of solvates from extractant molecules and fully dissociated inorganic compounds are considered): R_3NHNO_3 (I), $R_2SO.HNO_3$ (II); $RPO.HNO_3$ (III); $R_2N(CO)CH_3.HNO_3$ (IV); $R_3NHNO_3.HNO_3$ (V); $R_iNH_{4-i}.HCl$ (VI); $UO_2(NO_3)_2.2R_2SO$ (VII); $UO_2(NO_3)_2.2R_3PO$ (VIII); $UO_2(NO_3)_2.3[R_2P(O)O]_2CH_2$ (IX); $UO_2(NO_3)_2.R_3NHNO_3$ (X); $UO_2Cl_2.2R_3PO$ (XI); $UO_2[R_2P(O)O]_2$ (XII); $Pu(NO_3)_4.2R_3PO$ (XIII); $Pu(NO_3)_4.2(R_3NHNO_3)$ (XIV); $Ce[R_2P(O)O]_5$ (XV); $(R_3NH)_2M(NO_3)_5$ (M = Am, Cm, or Es) (XVII); $MCl_2.2R_3NHCl$ (M = Co or Zn) (XVII); $MCl_4.2R_3NHCl$ (M = Pu or Np) (XVIII); $Np(NO_3)_4.2R_3NHNO_3$ (XIX).

Table 1. Parameters characterising the inductive and steric effects of substituents*.

No.	Group	σ*	σp	E_s^*	No.	Group	σ*	σp	E_s^*
1	H	0.49	0.00	1.24	33	C_6H_5	0.60	−0.48	(−0.79)
2	CH_3	0.00	−0.96	0.00	34	$C_6H_5CH_2$	0.22	−0.69	−0.38
3	C_2H_5	−0.10	−1.10	−0.01	35	$C_6H_5(CH)_2$	0.07	−1.06	−0.38
4	C_3H_7	−0.115	−1.18	−0.04	36	$C_6H_5(CH)_3$	0.02	—	−0.43
5	C_4H_9	−0.13	−1.22	−0.10	37	$C_6H_5(CH)C_2H_5$	0.03	—	−0.28
6	iso-C_4H_9	−0.13	−1.30	−0.93	38	$C_6H_5(CH)CH_3$	0.12	—	−0.51
7	C_5H_{11}	−0.16	−1.21	−0.15	39	C_3H_5O	0.64	—	—
8	iso-C_5H_{11}	−0.16	−1.27	−0.40	40	p-$CH_3OC_6H_4$	—	−0.59	—
9	C_6H_{13}	−0.15	−1.21	−0.21	41	m-$CH_3OC_6H_4$	—	−0.53	—
10	C_7H_{15}	−0.15	−1.28	−0.29	42	p-$CH_3C_6H_4$	—	−0.22	—
11	C_8H_{17}	−0.16	−1.11	−0.33	43	m-$CH_3C_6H_4$	—	−0.66	—
12	iso-C_8H_{17}	−0.16	—	−0.39	44	p-ClC_6H_4	(−0.67)	−0.29	(−1.24)
13	C_9H_{19}	−0.16	—	−0.35	45	m-ClC_6H_4	—	−0.22	—
14	$C_{10}H_{21}$	−0.16	—	−0.37	46	p-BrC_6H_4	—	−0.25	—
15	$C_{12}H_{25}$	−0.165	−1.24	−0.40	47	m-BrC_6H_4	—	−0.23	—
16	$C_{14}H_{29}$	−0.16	—	−0.43	48	p-$CF_3C_6H_4$	—	−0.11	—
17	$C_{16}H_{33}$	−0.16	—	−0.46	49	m-$CF_3C_6H_4$	—	−0.15	—
18	$C_{18}H_{37}$	−0.16	—	−0.50	50	$(CH_3)_2N—C_6H_4$	—	−0.68	—
19	CH_3O	—	−0.12	—	51	1,1,3,3-Tetramethylbutyl	(−0.16)	—	(−0.81)
20	C_2H_5O	—	−0.21	—					
21	C_3H_7O	—	−0.32	—	52	1,1,1-Trialkylmethyl**	−0.16	—	−1.78
22	C_4H_9O	—	−0.41	—					
23	$C_5H_{11}O$	—	−0.39	—	53	2-Butylhexyl	(−0.16)	—	(−1.34)
24	$C_6H_{13}O$	—	−0.40	—	54	1-Isobutyl-3,5-dimethylhexyl	(−0.16)	—	(−1.38)
25	$C_7H_{15}O$	—	−0.45	—					
26	$C_8H_{17}O$	—	−0.50	—					
27	$C_9H_{19}O$	—	−0.52	—	55	p-$C_2H_5OC_6H_4$	(0.28)		(−0.64)
28	$C_{10}H_{21}O$	—	−0.46	—	56	$R_2P(O)CH_2$	0.56	—	—
29	$C_{12}H_{25}O$	—	−0.52	—	57	$Rh_2P(O)CH_2$	0.58	—	—
30	cyclo- C_6H_{11}	−0.17	−1.19	−0.79	58	cyclo-$C_6H_{11}NH$	—	(1.36)	—
31	cyclo- $C_6H_{11}CH_2$	−0.06	—	—	59	$C_6H_{13}NH$	—	(1.32)	—
32	cyclo- C_5H_{11}	−0.23	—	−0.51	60	C_4H_9NH	—	(1.33)	—

The values of σ are based in Refs. 26, 29, 52, and 53, those of σp are based on data in Refs. 44 and 54–56, and those of E_S^* are based on data in Ref. 52. In certain extraction studies[48] use was made of the parameters X = 2.07 + 0.5σ*; the parameters σp are related to σ* by the equation[55] σp = −0.965 + 1.97σ*. The values of E_S^* which agree with the corresponding parameters E_S [26] are underlined; values which have been tested in relation to a small number of systems are enclosed in brackets in this and subsequent Tables.

**The total number of carbon atoms in the three alkyl chains is 13.

The constants in Table 2 for approximately 400 of the extraction systems examined are expressed with the aid of 36 correlation equations. As will be shown in Section IV, the value of these equations consists not only in the abbreviation of the information, but also in the possibility of discovering new relations and predicting the extraction capacity of compounds which have not yet been investigated.

Table 2. Abbreviated expressions for the equilibrium constants for series of extraction reactions of the same type (only the nature of the substituents in the extractant molecules varies within the limits of the series).

Solvate*	Substituent** R in the extractant molecule	Diluent	Expressions*** for lg K	Refs.
(I)	$(9)_3$, $(11—15)_3$, (2,11,11), (34,11,11), (34,34,11—13), (9,9,34)	*o*-Xylene	$5.0-3.5\,\Sigma\,\sigma^*+$ $+1.55\,\Sigma\,E_s^*$	52, 57
(II)	$(10)_2$, $(33)_2$, $(42)_2$, (14,34)	C_6H_6 CCl_4 $CHCl_3$	$-0.63-0.92\,\Sigma\,\sigma^*$ $-1.03-0.68\,\Sigma\,\sigma^*$ $-1.49-0.55\,\Sigma\,\sigma^*$	58
(III)	$(7)_3$, $(9)_3$, $(12)_3$, $(28)_3$, $(28)_3$, (11,11,26), (7,7,19)	C_6H_6 CCl_4 $CHCl_3$	$-1.48-0.66\,\Sigma\,\sigma_p$ $-1.68-0.58\,\Sigma\,\sigma_p$ $-2.43-0.58\,\Sigma\,\sigma_p$	58, 59
	$(11)_3$, $(22)_3$, $(58—60)_3$, (8,8,2), (58,22,22), (58,25,25)	$CHCl_3$	$-2.13-0.56\,\Sigma\,\sigma_p$	60
	$(11)_3$, $(33)_3$, (56—57,33,33), (56,11,11), (56,5,5), (3,33,33)	$C_2H_4Cl_2$	$0.827-0.524\,\Sigma\,\sigma^*$	61
(IV)	$(11)_2$, $(14—15)_2$	*o*-Xylene	$0.73+1.57\,\Sigma\,\sigma^*+$	62
(V)	$(10—11)_3$, $(14—18)_3$, $(32)_3$, (15,15,34), (13,13,34), (4—5,11,11), (32,14,14), (38,11,11)	*o*-Xylene	$-0.22-0.27\,\Sigma\,\sigma^*+$ $+0.78\,\Sigma\,E_s^*$	52
(VI)	$(11)_3$, $(15)_3$, (13,13,34), (1,14,15), (2,2,18), (1,15,51), (1,12,52—54), (1,1,52)	Toluene	$6.46-0.76\,\Sigma\,\sigma^*+$ $+1.93\,\Sigma\,E_s^*$	52
(VII)	$(10)_2$, $(33)_2$, $(42)_2$ (14,32)	C_6H_6 CCl_4 $CHCl_3$	$2.68-1.55\,\Sigma\,\sigma^*$ $2.19-1.31\,\Sigma\,\sigma^*$ $1.48-0.88\,\Sigma\,\sigma^*$	63, 64
(VIII)	$(11)_3$, $(22)_3$, $(26)_3$, (11,26,26)	C_6H_6 CCl_4 $CHCl_3$	$-0.68-2.36\,\Sigma\,\sigma_p$ $-1.30-2.19\,\Sigma\,\sigma_p$ $-2.73-1.98\,\Sigma\,\sigma_p$	63, 64
	$(58—60)_3$, (25,25,58) (22,22,58), (22,58,58)	$CHCl_3$	$-0.928-\Sigma\,\sigma_p$	65
(IX)	$(16)_4$ $(30)_4$, $(42—50)_4$	$CHCl_3$	$7.34-0.66\,\Sigma\,\sigma_p$	66
(X)	$(10—15)_3$, (1,1,14), (1,11,11), (1,14,14), (1,15,15), $(11)_4$	CCl_4	$1.0-1.95\,\Sigma\,\sigma^*$	67
(XI)	$(11)_3$, $(22)_3$, (11,11,26), (2,23,23)	CCl_4	$0.2-0.92\,\Sigma\,\sigma^*$	68, 69
(XII)	$(5)_2$, $(7)_2$, $(9—14)_2$, $(19—29)_2$, (25, 34), (22,26)	C_6H_6	$2.96-0.80\,\Sigma\,\sigma_p$	54
(XIII)	$(5)_3$, $(22)_3$, (3—4,22,22), (7,22,22), (34,22,22), (2,28,28), (5,5,22)	CCl_4	$1057-2544\,\Sigma\,\sigma^*+$ $+120\,\Sigma\,E_s$	49
(XIV)	$(11—18)_3$, (2,14,14), (32,14,14), (34,18,18), (34,34,16—17), (34—36,15,15), (2,34,18), (38,11,11)	*o*-Xylene	$7.98-0.40\,\Sigma\,\sigma^*+$ $+2.24\,\Sigma\,E_s^*$	70
	$(11—16)_3$, (34,34,11)	CCl_4	$7.56-0.77\,\Sigma\,\sigma^*+$ $+2.15\,\Sigma\,E_s^*$	70
(XV)	$(5—6)_2$, $(9—14)_2$, $(19—29)_2$, $(33)_2$; (29,25), (22,26)	C_6H_6	$2.97+2.55$	64
(XVI)	$(11)_3$, $(14—16)_3$, (2—10,11,11), (33,11,11), (55,11,11), (33,33,14), (5,2,14), (2,14,7), (2,14,8), (2,14,14)	Xylene	$-0.21-1.06\,\Sigma\,\sigma^*+$ $+1.02\,\Sigma\,E_s^*$ (Am) $-0.60-1.25\,\Sigma\,\sigma^*+$ $+0.99\,\Sigma\,E_s^*$ (Cm) $-0.55-2.28\,\Sigma\,\sigma^*+$ $+1.04\,\Sigma\,E_s^*$ (Es)	71—73
(XVII)	(11,11,4), (11,11,34—36)	*p*-Xylene *p*-Xylene CCl_4	$0.20-1.6\,\Sigma\,\sigma^*$ (Co) $1.05-0.95\,\Sigma\,\sigma^*$ (Zn) $0.95-0.15\,\Sigma\,\sigma^*$ (Zn)	5
(XVIII)	$(14—18)_3$	*o*-Xylene	$5.8-8.0\,\Sigma\,E_s$ (Pu) $5.1-19.0\,\Sigma\,E_s$ (Np)	70
(XIX)	$(11)_3$, $(14—17)_3$	*o*-Xylene	$8\;27+2.9\,\Sigma\,E_s$	5

*The notation used for the solvates (denoted by Roman numerals) and the reactions leading to their formation is explained in the text (Section III, subsection 2).

**The substituents are designated by ordinal numbers corresponding to those in Table 1; the subscript indicates the number of substituents in the molecule.

***In cases (I)-(XII) expressions are given for lg$K$, in case (XIII) an expression for ΔG is given, and in the remaining instances the expressions are for the values of lg$D$, determined under standard conditions for each series.

By analogy with organic chemistry, one may also expect the validity of linear correlations between the logarithms of extraction constants and the steric constants of substituents for series where the inductive effects of the substituents vary little. Such correlations have also been obtained in a number of studies[70]. The correlations would embrace a wider range of extractants, if they related lg$K$ simultaneously to σ^* and E_S. However, only a small proportion of the available data have been interpreted in terms of the equation lg$K = f(\sigma^*, E_S)$. This can be explained by the lack, until recently, of a sufficiently complete scale of parameters E_S and partly by the inadequate number of measured constants for extraction by extractants having different structures. An attempt to extend the E_S scale has been made recently[52]. Analysis showed that the known values of E_S for alkyl groups ranging from CH_3 to C_6H_{13} are clearly inconsistent with experimental extraction data. For example, the replacement of the alkyl group in amines of the type $(C_8H_{17})_3NR$ in the sequence CH_3, C_2H_5,..., C_6H_{13}, C_8H_{17} entails a monotonic decrease of the extraction capacity; the logarithms of extraction constants vary linearly with the number of carbon atoms in the group. The parameters E_S initially increase from CH_3 to C_4H_9 and then decrease to C_6H_{13}, after which they increase once again. This made it necessary to develop a special scale of steric parameters E_S^* obtained from extraction data. It was based on the known values of E_S for hydrogen atoms, the CH_3 and C_8H_{17} groups, and certain others (in this region the E_S^* scale coincides with the E_S scale)[52].

Table 2 shows that, for identical series of systems with different diluents, the dependence of lg$K$ on σ is expressed by different equations; for a further condensation of information, it is therefore necessary to examine the possibility of deriving LFE equations which also take into account the influence of the nature of diluents.

The influence of the nature of the diluent. A linear correlation between the logarithms of extraction constants and parameters characterising the nature of the diluent was first demonstrated[74] in 1967, but the majority of diluents for which the corresponding parameters had been determined by that time in organic chemistry[75] are soluble in water. For this reason, the authors[74] developed a new scale of parameters applicable to diluents most frequently employed in extraction. The corresponding parameters were designated by ID (an abbreviation for the influence of the diluent). The validity of the equation lg$K$ = lgK_0 + aID was demonstrated[74] for 16 series of extraction systems (the majority of the series included 20-25 diluents each). Soon the validity of LFE with account taken of the influence of the nature of the diluent was demonstrated also in another study[15]. Subsequently the applicability of LFE to the prediction of the influence of the nature of the diluent was established experimentally for a large number of systems[5]. The parameters ID are listed in Table 3; Table 4 summarises the correlations discovered for extraction reactions leading to the formation of the following extractable compounds: diheptyl sulphoxide.HNO_3 (XX); trioctylphosphine oxide.HNO_3 (XXI); (trioctylphosphine oxide)$_2$.$HClO_4$ (XXII); trioctylphosphine oxide)$_2$.$HReO_4$ (XXIII); (trioctylphosphine oxide)$_2$.$HAuCl_4$ (XXIV); $[(C_8H_{17})_3NH]_2M(NO_3)_6$ [M = Pu (a) or Th (b)] (XXV); $[(C_8H_{17})_3NH]_2Bi(NO_3)_5$ (XXVI); $[(C_{12}H_{25})_3NHNO_3]$.HNO_3 (XXVII); $[(C_8H_{17})_3NHNO_3]$.HNO_3 (XXVIII); $[(C_{12}H_{25})_3N]$.HCl (XXIX), dioctylacetamide.HNO_3 (XXXa), didecylacetamide.HNO_3 (XXXb); dilaurlyacetamide.HNO_3 (XXXc); C_8 - C_{12} dialkylacetamides.HNO_3

(XXXd); (di-isobutyloctylamine H)$_2$.M(NO$_3$)$_5$ [M = Nd (XXXIa) or Dy (XXXIIb)]; (amine H)$_2$.ZnCl$_4$ [amine = $(C_8H_{17})_3N$ (XXXIIa)], $(C_{10}H_{21})_3N$ (XXXIIb), $(C_{12}H_{25})_3N$ (XXXIIc), LA-1 (XXXIId), LA-2 (XXXIIe); $[(C_{12}H_{25})_3NH]_2.$ $.Am(NO_3)_5$ (XXXIIIa); $[(C_8H_{17})_3NH]_2Am(NO_3)_5$ (XXXIIIb); $[(C_8H_{17})_3NH]_2ZnBr_4$ (XXXIV); $[(C_8H_{17})_3NH]_2CoCl_4$ (XXXV); $[(C_8H_{17})_3NH]FeCl_4$ (XXXVI); $[(C_8H_{17})_3NH]_2MoO_2Cl_4$ (XXXVII); $[(iso\text{-}C_5H_4O)_2(CH_3)PO]_2.FeCl_3$ (XXXVIII); $[(C_8H_{17})_3NH]_2.$ $.UO_2Cl_4$ (XXXIXa); $[(C_8H_{17})_2NH_2]UO_2Cl_4$ (XXXIXb); $[(C_8H_{17})_3NH]_2CoCl_4$ (XLa); $[(C_8H_{17})_2NH_2]_2CoCl_4$ (XLb); $[(C_8H_{17})_3NH]M(SCN)_4$ [M = Am (XLIa) or Ce (XLIb)].

Table 3. The parameters ID.

No.	Diluent	ID	No.	Diluent	ID
1	Cyclohexane	0.50	22	85% *n*-$C_{10}E_{22}$ + 15% $CHCl_3$	—1.12
2	Cyclohexane + C_6H_6 (1 : 1)	0.20	23	80% *n*-$C_{10}H_{22}$ + 20% $CHCl_3$	—1.47
3	*n*-$(CH_3)_2C_6H_4$	0.10	24	90% *n*-$C_{14}H_{30}$ + 10% $CHCl_3$	—0.75
4	*n*-$(C_2H_5)_2C_6H_4$	0.12	25	85% *n*-$C_{14}H_{30}$ + 15% $CHCl_3$	—1.07
5	$(C_2H_5)_3C_6H_3$	(—0.26)	26	80% *n*-$C_{10}H_{22}$ + 20% $C_8H_{17}OH$	—2.20
6	*o*-(iso-$C_3H_7)_2C_6H_4$	0.25	27	Cyclohexane + 1% $C_8H_{17}OH$	(0.53)
7	*o*-Xylene	0.12	28	Cyclohexane + 2% $C_8H_{17}OH$	(0.57)
8	Toluene	0.03	29	Cyclohexane + 3% $C_8H_{17}OH$	0.43
9	Benzene	0.00	30	Cyclohexane + 4% $C_8H_{17}OH$	(0.38)
10	Chlorobenzene	—0.15	31	Cyclohexane + 6% $C_8H_{17}OH$	(0.30)
11	Bromobenzene	—0.30	32	Cyclohexane + 10% $C_8H_{17}OH$	(0.23)
12	Bromobenzene + CCl_4 (1 : 1)	—0.50	33	Cyclohexanone	(0.3)
13	Chloroform	—1.52	34	n-Hexane + 4% $C_8H_{17}OH$	(0.12)
14	95%C_6H_6+5%$CHCl_3$	—0.40	35	Anisole	(0.18)
15	90%C_6H_6+10%$CHCl_3$	—0.65	36	Bromocyclohexane	(—0.45)
16	85%C_6H_6+15%$CHCl_3$	—0.90	37	1,2-Dichloroethane	(—1.75)
17	80%C_6H_6+20%$CHCl_3$	—1.20	38	Nitrobenzene	(0.86)
18	90% *n*-C_8H_{18} + 10% $CHCl_3$	—0.77	39	Octane	(0.20)
19	85% *n*-C_8H_{18} + 15% $CHCl_3$	—1.23	40	Carbon tetrachloride	—0.60
20	80% *n*-C_8H_{18} + 20% $CHCl_3$	—1.40	41	Butylbenzene	(—0.22)
21	90% *n*-$C_{10}H_{22}$ + 10% $CHCl_3$	—0.80	42	95% C_6H_6 + 5% $C_{10}H_{21}OH$	(—0.20)

Table 4 shows that the dependence of lg*K* on ID, represented by an equation of type (1), has been confirmed in more than 200 systems. A characteristic feature of these systems is that elements at microconcentrations, or concentrations which were small compared with that of the extractant, were extracted; the extractant concentration was low compared with that of the diluent. Another feature was the absence of the simultaneous extraction of the acid and the metal salt, i.e. only one component was partitioned in the system; in such cases the partition coefficients of an element measured under identical conditions for a given series are proportional to the extraction constants and correlations hold also for partition coefficients measured under standard conditions. For systems where an acid is extracted appreciably together with the metal salt, there should be no correlation between the partition coefficients and the ID. In such series one may expect only correlations between lg*K* and ID.

Examination of certain equations relating lg*K* to the parameters σ of substituents (Table 2) for series differing in the nature of the diluent [(II), (III), (VII), (VIII), (XVII)] shows that the constants of the equations and the sensitivity coefficients can also be represented by linear functions of the parameters ID of the diluent. This makes it possible to reduce several equations to a single expression taking into account the influence of both the structure of the extractant and of the nature of the diluent. For example, data for the extraction of uranyl nitrate by sulphoxides of different structure in benzene, carbon tetrachloride, and chloroform [see (VII), Table 2] can be represented with a high degree of accuracy[85] by the equation $\lg K = 2.68 - 1.55\,\Sigma\sigma^* + 0.80\,ID - 0.44\,ID\Sigma\sigma^*$. It is seen from the three equations for (XXXa)-(XXXc) in Table 4 that the change in their coefficients when the structure of the amide is altered takes place in conformity with the changes in E_a^*. Calculations demonstrated the possibility of expressing data for nine systems (three amides, three diluents) by the single equation $\lg K_{HA} = 0.68 + 1.00\,\Sigma E_s^* + 0.065ID$. In the examples presented above the decrease of the number of symbols expressing the available information is insignificant, but these examples demonstrate the fundamental pathway to a further condensation of information.

Table 4. Abbreviated expressions for the equilibrium constants for series of extraction reactions of the same type (only the nature of the diluent is varied within the limits of each series).

Solvate*	Diluent**	Expression for lg *K****	Refs.
(XX)	9,13,40	0.10+0.45ID	76
(XXI)	9,12,40	0.83+0.74ID	77
(XXII)	9,12,40	2.50+1.29ID	77
(XXIII)	9,13,39, 40	3.0+1.4ID	78
(XXIV)	1,9,13,40	6 3+1.2ID	78
(XXV)	2,3,8,10, 12—17, 23—26,40	a) 0 27+0.9ID b) —0.63+1.4ID	79
(XXVI)	2,3,8,9, 11,41	0.45+1.66ID	80
(XXVII)	3,9,11,40	—0.96+0.09ID	81
(XXVIII)	2,3,10,17	—0.86+0.17ID	81
(XXIX)	1,9,40	—3.9+0.48ID	81
(XXXa)	9,11,40	—0.32+0.65ID	82
(XXXb)	»	—0.42+0.65ID	»
(XXXc)	»	—0.52+0.65ID	»
(XXXIa)	8—9.42	1.25+2.5ID	83
(XXXIb)	»	1.15+3.0ID	»
(XXXIIa)	1—26.40	0.25+1.00ID	74
(XXXIIb)	»	1.17+1.10ID	»
(XXXIIc)	»	0.10+1.20ID	»
(XXXIId)	»	0.78+1.02ID	»
(XXXIIe)	»	0.85+1.13ID	»
(XXXIIIa)	1.6—9.33	0.12+2.50ID	84
(XXXIIIb)	»	0.12+3.20ID	»
(XXXIV)	1—26.40	—0.80+1.20ID	74
(XXXV)	1—26.40	0.50+1.27ID	74
(XXXVI)	1,2.9,14—16,22,23	0.20+1.15ID	74
(XXXVII)	9,14—16, 22,23	1.00+1.67ID	74
(XXXVIII)	1,9,14—16	0.50+0.87ID	74
(XXXIXa)	1.8—10.40	1.30+1.14ID	74
(XXXIXb)		—0.50+0.24ID	»
(XLa)	1.8—10.40	1.90+0.89ID	74
(XLb)	»	1.50+0.40ID	»
(XLIa)	1.9,40	1.80+0.33ID	74
(XLIb)	»	—0.20+2.60ID	»

*The notation for the solvates (indicated by Roman numerals) and the reactions leading to their formation is explained in the text (Section III, subsection 2).

**The diluents are designated by ordinal numbers corresponding to those in Table 3.

***In cases (XX)-(XXIV) and (XXVII)-(XXIX) the expression for lg*K* are quoted and in the remaining cases the expressions represent the values of lg*D* measured under identical conditions for each series.

Analysis of the linear relations between lg*K* and ID (Table 4) shows that they hold only for addition or double bond formation reactions which do not involve appreciable changes in the polarity of the components. In those cases where the polarity is altered appreciably, for example, in extraction via neutralisation or ion-exchange reactions, it is necessary to introduce another scale of parameters of the diluents[81], the so-called ID* scale (Table 5) in a quantitative description of experimental data. The use of this scale also made it possible to find many correlations of the type $\lg K = \lg K_0 + a\,ID^*$ (Table 6) for amine neutralisation reactions leading to the formation of the following compounds: $(C_8H_{17})_3NHCl$ (XLII); $(C_{12}H_{25})_3NHCl$ (XLIII); $(C_6H_5CH_2)_2(C_2H_{25})NHCl$ (XLIV); $(C_6H_6CH_2)\cdot(C_9H_{19})_2NHCl$ (XLV), $(C_8H_{17})_3NHBr$ (XLVI); $(C_{12}H_{25})_3NHBr$ (XLVII); $(C_8H_{17})_3NHI$ (XLVIII); $(C_{12}H_{25})_3NHI$ (XLIX); $(C_{12}H_{25})_2NHSCN$ (L); $(C_{12}H_{25})_3NHClO_4$ (LI); $(C_6H_5CH_2)\cdot(C_9H_{19})_2NHClO_4$ (LII); $(C_6H_5CH_2)_2(C_{10}H_{21})NHClO_4$ (LIII); $(C_8H_{17})_3NHNO_3$ (LIV); $(C_6H_5CH_2)_2(C_{10}H_{21})NHNO_3$ (LV); $(C_6H_5CH_2)(C_9H_{12})_2NHNO_3$ (LVI); for anion-exchange reactions leading to the formation of salts of the following type: $(C_{12}H_{25})_3NHReO_4$ (LVII); $(C_8H_{17})_3NHCl$ (LVIII, LX); $(CH_3)_2(C_{12}H_{25})NTcO_4$ (LIX); $(C_8H_{17})_3NCH_3COOH$ (LXI); for reactions involving the formation of neutral salts from alkylphosphoric acids: dioctylphosphoric acid with Er^{3+} (LXII) and Tb^{3+} (LXIII); di-2-ethylhexylphosphoric acid with Am^{3+} (LXIV), Cr^{3+} (LXV), UO_2^{2+} (LXVI), VO^{2+} (LXVII), Mn^{2+} (LXVIII), Zn^{2+} (LXIX), Cd^{2+} (LXX), Co^{2+} (LXXI), Ni^{2+} (LXXII), Ba^{2+} (LXXIII), Sr^{2+} (LXXIV), Cs^+ (LXXV), Ag^+ (LXXVI), neutral salts formed with thenoyltrifluoroacetone and solvated by tributyl phosphate (TBP), and salts with Pm^{3+} (LXXVII), Am^{3+} (LXXVIII), and Ce^{3+} (LXXIX).

Table 5. The ID* parameters.

No.	Diluent	ID*	No.	Diluent	ID*
1	n-Hexane	-0.6	14	*o*-Dichlorobenzene	2.0
2	n-Heptane	-1.0	15	Chloroform	4.5
3	n-Octane	-0.9	16	Bromoform	4.0
4	n-Decane	(-1.04)	17	Anisole	2.9
5	2,2,4-Trimethyloctane	(-0.8)	18	Methylene chloride	4.0
6	Cyclohexane	0.50	19	Butyl ether	0.8
7	Benzene	2.30	20	Isobutyl methyl ketone	2.5
8	Toluene	1.80	21	2-Ethylhexanol	9.5
9	Trimethylbenzene	1.45	22	2-Nitropropane	4.3
10	Triethylbenzene	0.95	23	Octane + 10% octanol	2.9
11	Carbon tetrachloride	1.4	24	Dodecane + 6% octanol	2.3
12	Tetrachloroethylene	1.1	25	Nitrobenzene	4.3
13	Chlorobenzene	2.7	26	Xylene	(1.8)

Since it has been shown[14] that, for certain series of systems where there are linear relations between lg*K* and ID*, there are also linear relations between lg*K* and the solvent parameters E_T, which are known in organic chemistry, it follows that parameters of the ID* and E_T scales are presumably linear related. Indeed it has been observed[86-89] that the parameters of these scales are linked by the relation ID* = −12.4 + 0.43E_T. However, the majority of the values of ID* listed in Table 5 were derived from extraction data for diluents whose E_T parameters are unknown. The observed correlation between ID* and E_T has been confirmed only for a small number of diluents whose E_T values are known; in order to describe extraction data, it is therefore probably desirable to employ the ID* scale.

It is seen from the foregoing that two different scales of diluent parameters are required for different types of reactions, each applicable to a wide range of systems‡.

The influence of the nature of the anionic ligand. Two types of influence of anionic ligands (A) on extraction are possible as a function of the role of these anions in the formation of extractable compounds. The first type arises when the anion is a nucleophilic centre of the extractant to which the extracted compound becomes attached and hence the stability of the extracted compounds determines the nucleophilicity of the anion. The second type occurs when the anion does not form part of the extractant and enters only into the composition of the salt extracted from the aqueous phase. In this case the energy of hydration of the salt anions extracted from the aqueous phase has a decisive influence on the partition during extraction.

Table 6. Abbreviated expressions for the equilibrium constants for series of extraction reactions of the same type (only the nature of the diluent is varied within the limits of each series).

Solvate*	Diluent**	Expression for lg*K****	Refs.	Solvate*	Diluent**	Expression for lg*K****	Refs.
(XLII)	6,8,11, 23,25	2.46+1.50ID*	81	(LVIII)	6—8,11,15	0.2+0.3ID*	91
(XLIII)	6,7,11,15, 23,25,26	2.51+1.00ID*	81	(LIX)	6—8,15	0.75+0.3ID*	92
(XLIV)	11,15,23, 25—27	1.75+0.80ID*	81	(LX)	6—8,11,15	−0.75—0.02ID*	91
(XLV)	11,15,23, 25—27	1.70+1.36ID*	81	(LXI)	6—8,15	0.20+0.16ID*	91
(XLVI)	6—8,22,25	3.38+1.44ID*	81	(LXII)	2,4,6,7, 9,11,15, 16,18,19, 20,25,26	2.80—0.56ID*	91
(XLVII)	6,7,11, 15,25	3.15+1.11ID*	81	(LXIII)	2,4,6,7, 9,11,15, 16,17,19, 20,25,25	3.73—0.55ID*	
(XLVIII)	6—8,22,25	5.16+1.45ID*	81	(LXIV)	4,6—8	1.5—0.6ID*	91
(XLIX)	6,7,11, 15,25	3.10+1.34ID*	81	(LXV)	4,6,8,15	—3.1—0.3ID*	91
(L)	6,7,11, 15,25	4.03+1.88ID*	81	(LXVI)	6,8,11,15	3.0—0.35ID*	91
(LI)	7,9,10, 12—14	2.66+1.80ID*	81	(LXVII)	4,6—8,21	0.1—0.1ID*	
(LII)	11,15,23, 25,27	6.81+0.60ID*	81	(LXVIII)	4,7,8,15	—2.3—0.3ID*	91
(LIII)	11,15,23, 27	4.75+0.16ID*	81	(LXIX)	4,7,8,15	—1.2—0.1ID*	94
(LIV)	7,15,24— 26	3.05+0.75ID*	5	(LXX)	4,7,8,15	—2.1—0.5ID*	94
(LV)	11,15,23, 25—26	3.15+0.46ID*	5	(LXXI)	4,7,8,15	—4.3—0.7ID*	94
(LVI)	11,15,23, 25,26	2.82+1.35ID*	81	(LXXII)	4,7,8,15	—5.8—0.3ID*	94
(LVII)	1,6,10, 12—14, 17,45	2.60+1.78ID*	90	(LXXIII)	4,7,8,15	—4.3—0.5ID*	94
				(LXXIV)	4,7,8,15	—3.8—0.5ID*	94
				(LXXV)	4,7,8,15	—3.4—0.3ID*	94
				(LXXVI)	3,6,7,11, 15	41.08—0.27ID*	95
				(LXXVII)	6,7,15	5.1—1.4ID*	96
				(LXXVIII)	1,6,7,11, 15	1.34—1.11ID*	97
				(LXXIX)	1,6,7,11, 15	2.82—1.19ID*	97

*The notation for the solvates (designated by Roman numerals) and the reactions leading to them is explained in the text (see Section III, subsection 2).

**The diluents are designated by ordinal numbers corresponding to those in Table 5.

***In cases (LVIII), (LIX), (LX), and (LXXV)-(LXXVIII) the expressions for values of lg*D*, measured under identical conditions for each series, are given.

In the first case one may expect that more stable complexes are formed with participation of more nucleophilic anions. Indeed it has been established[5] that acids whose anions are more nucleophilic (basic) are more effectively extracted by amine salts with a common anion via the addition reactions§ AmineHA ⇌ AmineHAHA (for example,

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‡The validity of the observed correlations in the description of the influence of the nature of the diluent on extraction has recently been demonstrated also from the standpoint of thermodynamics[98].

§In such systems the influence of the hydration of the anions in the aqueous phase is probably a secondary factor, which does not exert a decisive influence on the partition.

HNO_3 is extracted more effectively than HCl). A scale of Edwards parameters[30] (H), characterising the nucleophilic properties of anions belonging to the class of hard bases, had been introduced earlier in organic chemistry. These parameters are related to the pK_a of the corresponding acids by the expression $H = pK_a + 1.74$, but they are more universal since they have been determined also for the strongest acids whose pK_a values lack significance. It has been suggested[99] that there is a possibility of a linear correlation between the logarithms of the extraction constants (for a series of extraction reactions where the equilibrium is determined by the nucleophilic properties of the anion) and the parameters H of the anionic ligands in the system. This hypothesis was confirmed initially[90,99] for a relatively small series of reactions of acids with their amine salts and then for a large number of reactions of acids[100]. The parameters of the nucleophilic properties of certain anions are listed in Table 7; the linear correlations between $\lg K$ and H, found for the formation of compounds of the type $(C_8H_{17})_3NHA.HA$ (LXXX), $[(C_8H_{17})_3NH].UO(A)_3$ (LXXXI), $[(C_8H_{17})_3NH]_2Pu(A)_6$ (LXXXII), and $[(C_8H_{17})_3NH]_2Np(A)_6$ (LXXXIII), are listed in Table 8.

Table 7. The H parameters.

No.	Anion A	H	No.	Anion A	H
1	Br^-	—6.0	6	$CClH_2COO^-$	4.6
2	Cl^-	—3.0	7	CCl_2HCOO^-	3.0
3	F^-	4.9	8	CCl_3COO^-	2.6
4	NO_3	0.4	9	SCN^-	1.0
5	CH_3COO^-	6.7	10	CF_3COO^-	2.0

Table 8. Abbreviated expressions for the equilibrium constants for series of extraction reactions of the same type (only the nature of the anionic ligand is varied within the limits of each series).

Solvate*	Anion**	Expression for $\lg K$	Refs.
(LXXX)	1,2,4,6—10	$-1.0+1.07H$	100
(LXXXI)	2,4,6,7,9,10	$-1.65+1.63H$	101
(LXXXII)	1,2,4,9	$6.1+1.4H$	102
(LXXXIII)	1,2,4,9	$5.5+1.4H$	102

*The notation for the solvates (designated by Roman numerals) and the reactions leading to their formation is explained in the text (see Section III, subsection 2).

**The anionic ligands A are designated by ordinal numbers corresponding to those in Table 7.

In extraction systems where the anion is not a functional group of the extractant, its influence is determined mainly by the nature of its properties in the aqueous phase. In such systems, partition is influenced mainly by the anion hydration energy. Evidently the higher the hydration energy of the extracted simple or complex anion, the smaller its capacity for extraction via an addition or anion-exchange reaction[103]. It has been shown for extraction via an addition reaction in relation to the extraction of monobasic acids by trioctylphosphine oxide (TOPO) [104] that extractability increases in the sequence $HClO_4 > HReO_4 > HNO_3 > HBr > HCl$, which corresponds to the sequence based on the decrease of the hydration energies of these acids in the aqueous phase. It was then shown in a series of investigations[105-107] and in an independent study[5] that this relation can also be expressed quantitatively in the form of a linear free energy relation. Thus linear relations have been demonstrated[5] between the logarithms of the constants for the extraction of acids via neutralisation reactions of the type Amine + H^+ + A^- $\rightleftharpoons$ AmineHA and the free energies and enthalpies of hydration of the anions A^-. Since the logarithm of the equilibrium constant for an anion exchange reaction ($\lg K_X^Y$) of the type AmineHA + X^- $\rightleftharpoons$ AmineHX + A^- is equal to the difference between the logarithms of the constants for the formation of the salts AmineHA and AmineHX by a neutralisation reaction, there are also linear relations between $\lg K_X^Y$ and the difference between the values of ΔG or ΔH for the anions undergoing exchange[5,105]. Table 9 presents the values of ΔG and ΔH for the hydration of anions[111] and Table 10 lists certain correlations between $\lg K$ and the parameters ΔG_{hydr} and ΔH_{hydr} found for neutralisation reactions leading to the formation of the salts $(C_8H_7)_3NHA$ [in nitrobenzene (LXXXIV), toluene (LXXXV), and cyclohexane (LXXXVI)], $(C_{12}H_{25})_3NHA$ (LXXXVII), (AmineLa-2)HA¶ (LXXXVIII), and (Amine-IMT)HA† (LXXXIX) and for anion-exchange reactions leading to the formation of $(CH_3)_2R_2NReO_4$ from salts of the type $(CH_3)_2R_2NA$ (XC) and of $(C_8H_{17})_{14}NA$ from $(C_8H_{17})_4NClO_4$ (XCI), from $[(C_8H_{17})_4N]_2PdCl_2$ (XCII), and from $(C_8H_{17})_4NOH$ (XCIII). The number of correlations of this type discovered is small because relatively few of the corresponding reactions have been investigated quantitatively.

Table 9. The values of ΔG and ΔH for the hydration of anions[111].

No	Anion	ΔG, kcal g-ion^{-1}	ΔH, kcal g-ion^{-1}	No	Anion	ΔG, kcal g-ion^{-1}	ΔH, kcal g-ion^{-1}
1	I^-	—64	—67	10	ClO_4^-	—50	—54
2	Br^-	—72	—76	11	$PdCl_4^{2-}$	—	0**
3	Cl^-	—79	—84	12	$PdBr_4^{2-}$	—	—9**
4	NO_3^-	—69	—74	13	$Pd(SCN)_4^{2-}$	—	—14**
5	OH^-	—111	—122	14	PdI_4^{2-}	—	—21**
6	CO_3^{2-}	—108	—95*	15	SCN^-	—	—74
7	SO_4^{2-}	—249	—30*	16	F	—107	—
8	MoO_4^{2-}	—	0.5*	17	CH_3COO^-	—100	—
9	WO_4^{2-}	—	0.1*				

*$\Delta H = \Delta H_{L^{2-}} - 2\Delta H_{OH^-}$.[112]

**$\Delta H = \Delta H_{PdL_4^{2-}} - \Delta H_{PdCl_4^{2-}}$.[113]

¶ LA-2 is the secondary amine N-lauryltrialkylmethylamine.

† IMT is the primary amine 1,1,1-trialkylmethylamine where the overall number of carbon atoms in the three alkyl chains is approximately 20.

In a quantitative description of the influence of the nature of the anions on extraction one must take into account the role of the anion in the given series of extraction reactions, i.e. one must distinguish the two possible types of influence of anions indicated above. For example, in the unusual case of extraction of an acid via addition to an amine salt incorporating the anion of another acid[108], the degree of extraction increases with increase of the parameter of the nucleophilic properties of the anion forming part of the extractant composition (the amine salt) and constituting its functional group; on the other hand, a change in the nature of the anion of the acid in the aqueous phase influences the extraction equilibrium in the sequence corresponding to the change in hydration energy and not the change in nucleophilic properties[109]. Only in certain specific instances are the hydration energy and the nucleophilicity correlated[110].

Table 10. Abbreviated expressions for the equilibrium constants for series of extraction reactions of the same type (only the nature of the anion is varied within the limits of each series).

Reaction series*	Anion**	Expression for lg K	Refs.
(LXXXIV)	1—3	$24.3+0.20\,\Delta G$	5
(LXXXV)	1—3	$20.7+0.20\,\Delta G$	5
(LXXXVI)	1—3	$18.8+0.20\,\Delta G$	5
(LXXXVII)	1—3	$15.9-0.17\,\Delta G$	5
(LXXXVIII)	1—3	$10.3-0.06\,\Delta G$	5
(LXXXIX)	1—3	$14.7-0.06\,\Delta G$	5
(XC)	1—4	$-3.20+0.17\,\Delta G$	5
(XCI)	5—8***	$1.95-0.14\,\Delta H'$	110, 113, 114
(XCII)	9—12****	$0.5\,\Delta H''$	110, 113, 114
(XCIII)	1—5,10,16,17	$1.45+0.13\,\Delta G$	106

*The notation used for the reactions (designated by Roman numerals) is explained in the text (see Section III, subsection 2).

**The anions are designated by ordinal numbers corresponding to those in Table 9.

***$\Delta H' = \Delta H_{A^{2-}} - 2\Delta H_{OH^-}$.[112]

****$\Delta H' = \Delta H_{PdA_4^{2-}} - \Delta H_{PdCl_4^{2-}}$.[113]

Examination of the equations listed in Table 10 [(LXXXIV)-(LXXXVI)], describing the influence of the nature of the anions on extraction via a neutralisation reaction shows that the change in the coefficient of the equations as the nature of the diluent is altered takes place in accordance with the ID* scale. Calculations showed the possibility of expressing the data for all nine systems (three anions and three diluents) indicated above [Table 10, (LXXXIV)-(LXXXVI)] by a single equation: $\lg K_{HA} = \lg K_0 + a\text{ID}^* + b\Delta G$.

The influence of the nature of the extracted cation. The influences of the nature of the cation forming part of the composition of the extracted compound on the extraction constants have been compared for a series of similar extraction systems (incorporating the same aqueous phase and forming extractable compounds with the same solvation numbers), differing only in the nature of the extractant or the diluent[62]. It was shown that, when a scale of IE ("influence of the element") parameters, proportional to the logarithms of the constants for the extraction of quadrivalent actinides by tri-n-octylammonium nitrates from nitrate solutions is constructed, a linear relation with these parameters is also found for the logarithms of the constants for the extraction of actinides by tributyl phosphate, dioctylacetamide, and certain other nucleophilic extractants. The possibility of a linear correlation of the type $\lg K = \lg K_0 + m\text{IE}$ has been confirmed by numerous examples in inorganic chemistry. A number of reaction series in which there is a correlation between lg$K$ and the nature of the element has been indicated for inorganic systems[42,43]. For example, when the nature of the element M is varied within Group II, a linear correlation is observed[43] between the free energies of series of reactions of two types: $MO + SO_3 = MO_4$ and $MO + N_2O_5 = M(NO_3)_2$. This shows that it is desirable to develop a scale of parameters IE which determine the influence of changes in the nature of the metal in series of extraction reactions.

The following values of IE have been adopted[62]: 1 for Pu(VI), ~13 for Pu(IV), ~3 for Np(IV), ~1.5 for Np(VI), 4.9 for Th(IV), and ~2.8 for U(VI). The limits of the applicability of equations of the type $\lg K = \lg K_0 + m\text{IE}$ have not yet been elucidated: the applicability of this equation has been tested for a small number of series‡.

It has been found for extraction of various elements in the form of cations by organic acids that, regardless of the type of extractant, there is a definite sequence of the capacities of the cations for extraction with formation of salts[115]; this is reflected in a sequence of pH values at which 50% extraction takes place ($pH_{1/2}$). A sequence of such capacities of the cations for extraction by acid extractants has been established[115] qualitatively: $Bi^{3+} > Te^{3+} > Ti^{3+} > Sn^{2+} > Sb^{3+} > Pb^{2+} > Ca^{3+} > Cr^{3+} > In^{3+} > Cu^{2+} > Al^{3+} > Y^{3+} \simeq Ce^{+} > Ag^{+} > Au^{3+} > Cd^{2+} > Zn^{2+} > Ga^{2+} > Ba^{2+} > Ni^{2+} > Cs^{+} > Rb^{+} > K^{+} > Ca^{2+} > Mn^{2+} > Mg^{2+} > Na^{+} > Li^{+}$. It may be that the IE parameters, which make it possible to express quantitatively the extraction constant data with the aid of LFE, can also be found for systems where extraction proceeds via a cation-exchange mechanism.

The influence of the concentrations of the components of the aqueous phase. As mentioned in Section II, the principal method adopted for taking into account the influence of the quantitative composition of the aqueous phase involved the use of LMA in combination with data for the activity coefficients, complex formation, and hydrolysis in the aqueous phase. These data may be calculated by analysing the deviations of the apparent extraction constants from the effective constant for different concentrations of the components of the aqueous phase. However, in many systems, where appreciable extraction of the elements takes place only at relatively high ligand concentrations, it is difficult to determine the effective constant by extrapolating the apparent constants to zero concentration. In this case models based on LFE may be useful for the calculation of the influence of the concentrations of the components of the aqueous phase.

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‡ Linear relations between lg$K$ and IE have been found[62] for the extraction of Pu(IV), Pu(VI), Np(IV), Np(VI), U(VI), and Th(IV) from nitrate solutions by the following extractants: tributyl phosphate, diheptylacetamide, dilaurylacetamide, and tri-n-octylammonium nitrate.

Indeed in those cases where only one component is extracted the relation between the logarithms of the partition coefficients and the concentration of the components of the aqueous phase for a series of systems with different qualitative and quantitative compositions of the organic phase are frequently expressed by parallel lines[116,117]. The relation $\lg D = \lg D_0 + \psi\text{IAP}$, where D_0 is the partition coefficient when the aqueous phase adopted as the standard is used, D is the partition coefficient for the given aqueous phase (all other parameters being unchanged within the limits of the series), IAP the parameter characterising the influence of the aqueous phase§ of given composition and independent of the type of extraction series, and ψ the sensitivity coefficient, which is constant within the limits of each extraction series, holds for systems of this kind[118]. The employment of IAP parameters may be useful in condensing information only in those cases where a large number of systems with the same aqueous phase have been investigated. Such systems include, for example, the Co^{2+}–HCl–H_2O–organic phase or UO_2^{2+}–HCl–H_2O–organic phase systems; for each system, the number of series investigated amounts to several tens. Table 11 lists the values¶ of IAP for certain systems calculated by the present author and Shesterikov[118]; Table 12 lists the expressions for the partition coefficients using these parameters, found[118] for extraction reactions leading to the formation of solvates: $(\text{AmineH})_2\text{CoCl}_2$ (XCIV), $(\text{AmineH})_2 . \text{ZrCl}_6$ (XCV), $(\text{AmineH})_2\text{PuCl}_6$ (XCVI), $(\text{AmineH})_2\text{UO}_2\text{Cl}_2$ (XCVII), and $(\text{AmineH})_2\text{PuO}_2\text{Cl}_4$ (XCVIII). Correlations between $\lg K$ and IAP for a large number of series (about 100) have been published[118,119].

Table 11. The values of IAP characterising the influence of the aqueous phase on the partition coefficients in the Co^{2+}, M^{4+}, MO_2^{2+}–HCl–H_2O–organic phase systems*.

[HCl], M	IAP			[HCl], M	IAP		
	Co^{2+}	MO_2^{2+}	M^{4+}		Co^{2+}	MO_2^{2+}	M^{4+}
2.0	−1.16	−1.26	—	6.0	1.27	0.40	5.88
3.0	−0.63	−0.50	−4.51	7.0	1.60	0.47	7.16
4.0	0.00	0.00	0.00	8.0	1.74	0.49	8.15
5.0	0.72	0.23	3.64	9.0	1.60	0.40	8.90

* $MO_2^{2+} = UO_2^{2+}$, NpO_2^{2+}, PuO_2^{2+}, MoO_2^{2+}, or WO_2^{2+}; $M^{4+} = Th^{4+}$, U^{4+}, Np^{4+}, Pu^{4+}, Zr^{4+}, or Hf^{4+}.

It is seen from Tables 2, 4, 6, 8, 10, and 12, that the use of the above scales of parameters σ^*, E_s^*, ID, ID*, H, IE, IAP, and ΔG_{hydr} may be useful for an abbreviated formulation of the experimental data for partition in various systems with the aid of equations of type (1) and also for the prediction of the influence of various factors on extraction. Equations of type (1) hold most precisely in those cases where the reaction series do not differ greatly from one another as regards the type of the interactions which determine the partition. For such systems, comparison of the equations derived makes it possible to discover certain general characteristics, which are less apparent when one considers experimental data which have not been interpreted with the aid of LFE. When there are significant differences between the mechanisms influencing partition in various series, deviations may be observed from type (1) equations, which yield valuable evidence about the characteristics of the mechanisms of the corresponding reactions. This makes it possible to employ LFE for the analysis of the changes in the properties of extraction systems under the influence of various factors[25].

Table 12. Abbreviated expressions for the partition coefficients for series of extraction systems (only the quantitative composition of the aqueous phase is varied within the limits of each series)[118,119].

Solvate*	HCl, M	Extractant and diluent	Expressions for $\lg D$
(XCIV)	4—10	0.1 M cyclohexyldi(n-dodecyl)-amine in benzene	−0.96+1.01 IAP
(XCV)	7—10	0.1 M tri-n-octylamine in benzene	−8.32+1.0 IAP
(XCVI)	3—9	0.047 M tri-n-octylamine in xylene	0.08+0.201 IAP
(XCVII)	3—10	0.023 M tri-n-octylamine in xylene	0.76+1.17 IAP
(XCVIII	3—10	0.023 M tri-n-octylamine in xylene	1.00+2.04 IAP

* The notation for the solvates (designated by Roman numerals) and the extraction reactions leading to their formation is explained in the text (see Section III, subsection 2).

IV. ANALYSIS ON THE BASIS OF LFE OF THE CHANGES IN THE PROPERTIES OF EXTRACTION SYSTEMS UNDER THE INFLUENCE OF VARIOUS FACTORS

1. The Influence of the Structure of the Extractant

For systems where equations of type (1) hold, it is of interest to analyse (by comparing the coefficients of these equations) the influence of the structure, the solvation number, and the type of functional group on the selectivity of the extractants. Examination of the sensitivity coefficient ρ, can also be used[26] to assess the nature of the bond between the extractant and the extracted compound in the extractable complex. For individual systems where there are deviations from Eqn. (1), analysis of these deviations may be used to estimate the characteristics of the interaction of the components in the extractable complex and to elucidate the role of other factors which influence partition.

The influence of the nature of substituents on selectivity. A general characteristic feature of the equations expressing the influence of σ and E_s on $\lg K$ in extraction by nucleophilic extractants is the

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§ IAP is the abbreviation for "influence of the aqueous phase".

¶ In constrast to all the parameters described above, the IAP parameters characterise the influence of a quantity which varies continuously and not discretely. It is therefore useful to represent the IAP scale also in the form of a function which can be fitted to the relation between IAP and [HA].

increase of the absolute sensitivity coefficients ρ and a with decrease of the capacity of the element for extraction by the given extractant with a specific functional group. Thus Table 2 [solvate (XVII)] shows that $\rho = -0.95$ for $ZnCl_2$, which is extracted by amines from hydrochloric acid solutions more effectively than $CoCl_2$, while $\rho = -1.60$ for $CoCl_2$; $a \simeq 2.2$ for $Pu(NO_3)_4$, which is extracted by amines from nitric acid solutions more effectively than $Np(NO_3)_4$ and $a \simeq 3$ for Np(IV) [Table 2, (XVIII), (XIX)]. Owing to these relations between the sensitivity coefficients, the difference between the abilities of the amines to extract cobalt(II) and zinc(II) from hydrochloric acid solutions increase with decrease of the positive inductive effects of substituents, i.e. with increase of the quantities $\Sigma\sigma^*$, and the difference between the abilities of the amines to extract plutonium(IV) and neptunium(IV) from nitric acid solutions increase with increase of steric hindrance by the substituents, i.e. with decrease of $\Sigma E^*_{\rm s}$. The following rule arises from this feature: for series of extraction systems differing only in the nature of the extracted metals but characterised by the same solvation numbers, the same composition of the extractable complex, and the same type of nucleophilic extractant, the selectivity in the extraction of the metals increases when the inductive and steric effects of the substituents change in such a way that the extraction capacity decreases, i.e. with increase of $\Sigma\sigma^*$ and with decrease of $\Sigma E^*_{\rm s}$.

This rule holds also in the extraction of tervalent transplutonic elements [Table 2, (XVI)]—for example, the extraction of americium nitrate by substituted ammonium nitrates takes place with higher partition coefficients than the extraction of curium and einsteinium and at the same time ρ for Am(III) is smaller than for Cm(III) and Es(III). This also applies to the extraction of lanthanide elements by amines from nitrate solutions. Certain deviations from the above rule indicate some unexplained features of the extraction of these elements, possibly a difference between the solvation numbers within the limits of the series [tervalent lanthanides are known[5] to be capable of extraction by amines both in the form of complexes having the composition $(AmineH)_2M(NO_3)_5$ as well as in the form of compounds of the type $(AmineH)_3M(NO_3)_6$].

The influence of the solvation number on selectivity. Other conditions being equal, an increase of the solvation number should lead to an increase of the absolute values of ρ and a. Indeed, if the formation of the disolvate is assumed to proceed via a stage in which a monosolvate is formed, then the overall equilibrium constant for the formation of the disolvate K should be equal to the product of the formation constant of the monosolvate K_1 and the constant for the formation of the disolvate from the monosolvate K_2. On the grounds of statistical considerations, one may expect that $K_2 = \frac{1}{2}K_1$, so that $K = \frac{1}{2}K_1^2$ or $\lg K = \text{const.} + 2 \lg K_1$. If $\lg K_1 = \text{const.} + \rho\Sigma\sigma^*$, then $\lg K = \lg K_0 + 2\rho\Sigma\sigma^*$, i.e. the sensitivity coefficient in Eqn. (1) for the formation of the disolvate may be approximately twice as large as for the formation of the monosolvate. Such influence of the solvation number on ρ permits the formulation of the following rule: if the extractable complexes of two elements in a given extraction system differ by their solvation numbers, then, when the nature of the substituents is altered in a way leading to an overall decrease of the extraction capacity (increase of $\Sigma\sigma^*$, decrease of $\Sigma E_{\rm S}$), the extraction selectivity falls if the element whose complex has a smaller solvation number is also distinguished by a lower capacity for extraction, and increases if the element is extracted more effectively than the element whose complex has a larger solvation number.

This rule apparently makes it possible to account for certain characteristics of the influence of the structure of amines on their selectivity in the extraction of the lanthanides. Thus it has been shown[120] that, on passing from trilauryl- or trioctyl-amine to dilaurylmethyl- or methyldioctyl-amines respectively, the partition coefficients of cerium and praseodymium in extraction from nitrate solutions increase; however, this change also entails an increase of selectivity, which is inconsistent with the rule quoted in the previous section. This discrepancy led Kopyrin et al.[120] to investigate in greater detail the stoichiometry of the extraction of the lanthanides by the above amines. It was found that, on passing from symmetrical pentylamines, forming disolvates of the type $(R_3NH)_2M(NO_3)_5$ with lanthanide nitrates, to dialkylmethylamines, the average solvation number increases owing to the extraction of part of the element in the form of a trisolvate of the type $(R_2CH_3NH)_3M(NO_3)_6$. In this case the trisolvates have a higher partition coefficient than the disolvates and, in conformity with the last rule, the partition coefficients of cerium and praseodymium increase on passing from symmetrical trialkylamines to dialkylmethylamines.

Analysis of deviations from a type (1) equation. Individual deviations from Eqn. (1) make it possible to determine the characteristics of the extraction reaction which are not taken into account in the selection of the initial data. For example, calculations showed that the use of the equation quoted in Table 2 [solvate (V)] leads to a satisfactory agreement between the calculated and experimental data for the substituents indicated in Table 2 (15 combinations), but, for certain other substituents (when the number of carbon atoms in the amine molecule is less than 18), the calculated data are somewhat higher than the experimental values, the discrepancy increasing with decrease of the number of carbon atoms[52]. This shows that, for amines, with insufficiently hydrophobic substituents, the stability of the extractable compound may no longer be regarded as the sole factor which determines the extraction constant, since the solubility of the compound in the aqueous phase also begins to have an influence, the solubility increasing with decrease of the total number of carbon atoms to values less than 18. The observed discrepancies between the experimental and calculated data can probably be used to estimate the solubility of the amine salt in the aqueous phase.

It has been shown[121,122] that the extraction capacities of certain tetra-arylmethylenediphosphine oxides in relation to americium nitrate deviate appreciably from values calculated by equations of type (1), which led the authors[122] to investigate in detail this anomalous system. Spectrophotometric study demonstrated the presence, apart from the usual P=O...Am linkages, of additional bonds between the aryl groups and the oxygen atoms of the nitrato-groups of the complex anion $Am(NO_3)_5^{2-}$ in the corresponding extractable complex.

The value of ρ and the type of bond in the extractable complex. The quantity ρ may indicate the type of bond in the complex formed on extraction (this refers primarily to the absolute value of ρ). A high absolute values of ρ is known[26] to indicate a large contribution of polar bonds to the formation of the complex, while a small absolute value indicates a predominantly homopolar nature of these bonds. The data in Table 2 show that ρ exceeds unity for the extraction of acids by amines by a neutralisation reaction, which indicates an appreciable contribution of polar bonds. In the extraction of HNO_3 by substituted ammonium nitrates via an addition reaction $\rho \simeq -0.2$, which indicates a large contribution by covalent bonds to the formation of compounds of the type [Amine.HNO_3]HNO_3. It is of interest to analyse also the sign of the coefficient ρ for series in which metals are extracted by chelate-forming extractants, for example, by alkylphosphoric acids. It was found that for these series the sign of ρ is negative, as for nucleophilic extractants of the type of phosphine oxides. This shows that the nucleophilic properties of the oxygen atoms and their ability to form electron-donor bonds with the metal cation have a decisive influence on the stability of the compounds extracted by acid phosphorus-containing extractants. The capacity of the acid for dissociation, the dependence of which on $\Sigma\sigma^*$ would involve a positive coefficient ρ, is evidently of secondary importance for extraction capacity in these systems. At the same time it is seen from Table 2 that in individual instances the sign of the sensitivity coefficient ρ for extraction by a series of acid organophosphorus extractants may be positive. Evidently in this case the role of nucleophilic interactions is small and the capacity of the acid extractant for dissociation plays a decisive role.

Comparison of the values of ρ for series of extraction reactions involving the functional groups $>S{=}O$, $>P{=}O$, or $>C{=}O$ makes it possible to estimate the change in the nature of the extractant–metal salt bonds in this series of groups.

2. The Influence of the Nature of Diluents

By analysing LFE equations, the characteristic features of the influence of the nature of the diluent on the relative strengths of various extractants and on the selectivity of extraction have been established[5,25].

The influence on the relative strengths of different extractants. Table 2 [(II), (III), (VII), (VIII), (XVII)] shows that, when electrophilic diluents (with low ID) are used, the degree of extraction via addition and complex formation reactions, which do not entail an appreciable change in the polarity of the components, diminishes, on the one hand, and the coefficients ρ in type (1) equations decrease, on the other. Because of this, the employment of diluents with low ID results in the abolition of differences between extractants of the same type having identical functional groups and variable substituents. This behaviour is also evident from a comparison of the equations presented in Table 4 [(XX), (XXI), (XXVI), (XXVIII), (XXX)]; evidently, in the extraction of HNO_3 by different extractants the coefficient of ID is lower the smaller the constant term in the equation. This leads to the mutual approach of the values of lg$K$ for extractants with different substituents and a constant functional group as ID decreases. Such behaviour is evident from a comparison of the equations for (XXXII) in Table 4 for the extraction of $ZnCl_2$ and for (XXXIX) and (XL) in Table 4 for the extraction of UO_2Cl_2 and $CoCl_2$ by extractants with different substituents. The following rule has been formulated on the basis of these observations[25]: the decrease of the parameter ID by the diluent has a levelling effect on the extracting capacities of different extractants which extract acids and metal salts via addition or complex formation reactions not involving a sharp change in the polarity of the components (i.e. those where the ID scale is applicable). Another type of behaviour is manifested in systems to which the ID* scale is applicable. Analysis of the data in Table 6 [(XLII)–(XLV) (for HCl); (XLVI), (XLVII) (for Hbr); (XLVIII), (XLIX) (for HI); (LIV), (LV) (for HNO_3)] show that the differences between the extracting capacities of extractants of different structure in such systems are apparently abolished with decrease of the solvating capacity of the diluents, i.e. with the decrease of the parameters ID*, because the coefficients of ID* in the equations for lg$K$ increase with increase of the constant in these equations. In contrast to the influence of ID, the last rule does not hold fully [for the deviations, see Table 6, (XLVI) (for HNO_3)].

The influence on extraction selectivity. The influence of ID depends on the ratio of the solvation numbers. The causes and nature of this influence are analogous to those described above for the influence of solvation numbers which the structures of the extractants are altered. With increase of the solvation number, the influence of the nature of the diluent on the partition coefficient (other conditions being equal) should be greater [cf. (XXII)–(XXIV) and (XXI), Table 4], which has a corresponding influence on the selectivity.

It is also of interest to compare the influence of the ID parameters on selectivity for identical solvation numbers of compounds of two elements being extracted. It is known that Pu(IV), Th(IV), and Bi(III) are extracted by trioctylammonium nitrate in the form of disolvates and their extractability from nitric acid solutions varies in the sequence Pu(IV) > Th(IV) > Bi(III). Comparison of (XXV) and (XXVI) in Table 4 shows that the sensitivity coefficients in the correlation equations vary in the opposite sequence. Thus the differences between the degrees of extraction of these elements will increase with decrease of ID, i.e. with the increase of the degree of specific solvation of the functional group of the extractant by the diluent.

Similar behaviour is also seen on comparing the degrees of extraction of Am(III) and Ce(III) by a substituted ammonium thiocyanate [(XLI) in Table 4], HCl and HNO_3 by their substituted ammonium salts [(XXVII) and (XXIX), Table 4], neodymium and dysprosium by a substituted ammonium nitrate [(XXXI), Table 4], and uranium(VI) and cobalt(II) by a substituted ammonium chloride [(XXXIXa), (XLa), (XXIXb), (XLb), Table 4]. Molybdenum(VI), cobalt(II), and zinc(II) are known to form the following sequence in terms of their capacity for extraction by tri-n-octylammonium chloride: Zn > Co > Mo. The sensitivity coefficients of the correlation equation increase in the opposite sequence also in the above series, which leads to an increase of selectivity with decrease of ID. One can therefore formulate the following rule: for systems where the influence of the diluent may be expressed by a dependence on ID, with identical solvation numbers of two extracted elements, the selectivity of the extraction by a given nucleophilic extractant increases with decrease of the ID parameter of the diluent, i.e. with increase of the ability of the diluent to solvate the nucleophilic functional group of the extractant.

Consider the influence of ID* on selectivity. Comparison of data for (XLII), (XLVI), and (XLVIII) as well as those for (XLIII), (XLVII), and (XLIX) in Table 6 shows that the selectivity in the extraction of hydrogen halides by trioctyl- and trilauryl amines via a neutralisation reaction decreases with increase of ID*, i.e. with increase of the solvating capacity of the diluent. Overall, an increase of ID* promotes extraction reactions leading to the formation of more polar compounds. Thus in anion-exchange by substituted ammonium salts an increase of ID* promotes the conversion of less polar substituted ammonium sulphates into more polar salts—chlorides and pertechnetates [see (LVIII) and (LIX) in Table 6] and the conversion of acetates into chlorides [see (LXI) in Table 6], but prevents the conversion of the more polar bromide into the less polar substituted ammonium chloride [see (LX)]. In extraction by acid extractants (in contrast to extraction by amines), an increase of ID* leads to a decrease of the degree of extraction. This probably indicates a lower polarity of the metal salts formed compared with that of the acid extractants. Under these conditions (for equal solvation numbers), the differences between the degrees of extraction of different elements are abolished with increase of ID* of the diluent: the absolute value of the negative sensitivity coefficient becomes smaller with decrease of the constant coefficient [see, for example, (LXIX), (LXX), and (LXXI), or (LXIV) and (LXV) in Table 6].

On the basis of the foregoing, one can formulate the following rules: (a) in anion-exchange reactions an increase of ID* greatly favours reactions leading to the formation of more polar compounds in the organic phase, i.e. an increase of ID* tends to increase the selectivity in the extraction of anions of stronger monobasic acids from a medium comprising weaker acids and the extraction of singly charged anions from a medium containing doubly-charged and multicharged anions; (b) in cation-exchange reactions an increase of ID* prevents the conversion of acids into metal salts and lowers the selectivity in the extraction of the latter[91].

3. The Influence of the Nature of the Anionic Ligand

A significant influence of the parameters H on selectivity in the extraction reactions of elements which are hard acids and have the same solvation numbers has not been observed [see, for example (LXXXII) in Table 8]. It is more likely to observe the influence of H in those cases where the formation of extractable compounds of different elements involves the addition of different numbers of anionic ligands; evidently, with increase of this number, the coefficient of the parameter H in the LFE equation [$\lg K = f(H)$] should also increase, which may lead to an alteration of the relative capacities of two such elements for extraction as the parameter H is changed.

The dependence of selectivity on H for the anionic ligand is manifested more clearly in those cases where one of the elements is a hard acid and the other is a soft acid. In this case an increase of H for the hard element leads to an increase of the degree of extraction and an increase of H for the soft element in most cases results in its decrease. For example, the degree of extraction of soft cadmium or cobalt(II) from halide media increases as the halogen is altered in the sequence $F < Cl < Br < I$, while the degree of extraction of hard zinc(II) decreases in the same sequence. (Zinc is appreciably extracted from a medium containing Cl^- anions, but is hardly extracted from a medium where iodide anions predominate[123].) On the other hand, the hard element zirconium(IV) is effectively extracted from an HF medium (at low HF concentrations), while soft cadmium(II) is hardly extracted from the same medium. One can therefore formulate the rule that, within certain limits, the parameter H has a decisive influence on the selectivity in the extraction of metal salts by substituted ammonium salts with the same anions: the extraction selectivity in relation to a pair of elements whose cations are hard and soft acids respectively may be increased by employing anions with higher values of H in those cases where the hard element is more effectively extracted or by employing anions with low values of H in those cases where the soft element is more effectively extracted.

The applicability of this rule is limited, because the sequence of the changes in the extractability of complexes of different anions for soft acids is not fully the opposite of the corresponding sequence (H scale) for hard acids. For example, the CN^- anion has a high value of H, but forms readily extractable complexes with elements whose cations are both hard and soft acids. In those cases where anions are extracted via anion-exchange reactions, the selectivity of extraction by a given extractant increases with increase of the difference between the free energies of their hydration in the aqueous phase (Table 9).

One should note certain limitations in the applicability of the rules and relations based on LFE. They are applicable in a general form to linear correlations involving the logarithms of extraction constants; they are applicable to partition coefficients only in those cases where the latter are proportional to the extraction constants, i.e. when the phase composition in terms of concentration is constant throughout the series. Such proportionality holds fully only at extractant concentrations much lower than diluent concentrations and at concentrations of the extractable compound much lower than the extractant concentrations. However, this does not diminish the generality of the method, because it is possible to extend, with the aid of the Law of Mass Action, data obtained subject to the above limitations to wider concentration ranges.

The data presented in the present review show that LFE together with LMA may be used to express in an abbreviated form large sets of experimental extraction data.

In order to be able to employ the above equations in reference compilations instead of numerous experimental data, it is extremely important to estimate the accuracy of the calculated results. In the first stages of the development of the application of LFE to extraction, investigators did not calculate quantitative parameters characterising the accuracy of the correlation (correlation coefficients, variances, average deviations). An approximate estimate shows that, for the majority of the equations quoted in the present review, the correlation coefficient is 0.9. It has now become a rule to give in extraction reports an estimate of the accuracy of the proposed correlation equations. Thus the correlation coefficient has been estimated as 0.98 in a study by Fedoezzhina et al.[58] [see (II), Table 2)] and Shmidt et al.[124] found that the average deviation of the calculated values of K from the experimental results amounted to approximately 10% when K varied by three orders of magnitude [see (XVI), Table 2]. It is necessary that in the future derivation of new correlation equations their accuracy should be estimated quantitatively in accordance with statistical requirements[125].

In essence the first steps have already been taken towards the condensation of information about extraction equilibria with the aid of LMA and LFE. Presumably in the future the need for this type of condensation will increase, which will lead to a wider employment of the methods described as well as their improvement. Equations based on LMA and LFE can also be used as instruments for discovering new characteristics of the extraction process and for the determination of the specific features of the behaviour of components in individual extraction systems.

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Coordination Chemistry in Italy: The Work of the Rome School

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The principal directions of the development of coordination chemistry in Italy (the Rome school) are considered in their historical aspect. In the field of the theory of the structure of complex compounds research on the ligand field theory and calculations by the molecular orbital methods are being carried out in Rome. Numerous studies on the synthesis and determination of the structures of many new complexes are examined and the kinetics and mechanisms of chemical reactions of coordination compounds, mainly substitution reactions, are discussed. Much attention is devoted to the investigation of the properties of complexes with the aid of various physical methods—electronic and photoelectron spectroscopy, vibrational spectroscopy, magnetic resonance methods (EPR, NMR, NQR), and electrochemical methods (particular polarography). Studies related to the preparation of catalytically active complexes and their properties are also considered.
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I. INTRODUCTION

Coordination chemistry has been very popular in Italy for a very long time. During the period when Werner developed intensive investigations in Zurich, Miolati in Padua studied the structure of polyacids. In the next decade Cambi, Natta, and other well known chemists carried out the first studies in the field of metal complexes. Soon after the second world war Italian scientists participated in the development of all the fields of modern coordination chemistry, so that at the present time studies on the coordination compounds are prosecuted in almost every Italian university. Several particularly active scientific centres arose, the most important of which are those in Milan, Padua, Florence, and Rome. The present review gives a brief historical description of the development of the Rome centre and also the results of scientific research carried out in the last few years and being prosecuted at the present time.

The work of Professor Vincenzo Caglioti, who laid the foundations of the Rome school during the war and in the subsequent years, has had the greatest influence on the development of coordination chemistry in Rome. These studies are now being continued by Prof. Guido Sartori and many of his coworkers, working both in the Rome University and in other Italian institutes. This review will therefore survey the results of research by the chemists in the Rome school working in more or less closely related fields at the following institutes: the Institute of General and Inorganic Chemistry at the Rome University; the Laboratory of the Theory of the Electronic Structures and Spectrochemical Properties of Coordination Compounds of the National Research Council of Italy in Rome; the Institute of General and Inorganic Chemistry at the Peruggia University. In addition, mention will be made of some of the studies carried out at the Chemical Institute of the University of Trieste.

II. PRINCIPAL FIELDS OF RESEARCH

Traditionally the work of the Rome school on coordination chemistry, which began in the 1930's with early polarographic studies[1-4], embraced a wide range of fields, including almost all the aspects of the chemistry of metal compounds—from the fundamental theory to problems of industrial applications. However, studies on the electronic structures, stereochemistry, spectroscopy, and related problems have developed to the greatest extent; thermodynamics and resonance spectroscopy have been less well developed. The consideration of various aspects of this research may be divided into eight sections:

(1) theory of the coordinate bond;
(2) syntheses of new coordination compounds and determination of their structures by X-ray diffraction analyses;
(3) kinetics of substitution reactions involving metal complexes;
(4) electronic spectroscopy;
(5) vibrational spectroscopy;
(6) electrochemistry;
(7) various research methods;
(8) applied research.

This subdivision is undoubtedly extremely arbitrary, some of the relevant studies being carried out simultaneously. For example, syntheses have been frequently performed in order to obtain complexes which might confirm theoretical principles; electrochemical studies in non-aqueous solvents made it possible to characterise and synthesise complexes unstable in an aqueous medium; X-ray diffraction studies went hand-in-hand with the spectroscopy of single crystals, etc.

III. THEORY OF COORDINATION BINDING

The interest of the Rome school in research on the nature of bonds in complexes arose in the 1950's when Hartmann's work[5] demonstrated the entire importance for chemistry of the crystal field model developed by Bethe[6], Van Vleck[7], and others and laid the foundations of the modern ideas about the coordinate bond. Early contacts of Italian chemists with Hartmann's group[8-10] ensured that the ligand field theory became widely known in Italy. This led to the appearance in 1957–1964 of a large number of publications devoted to the interpretation (from the standpoint of this theory) of the structures and spectra of complexes having a definite electronic configuration, particularly the d^6 configuration in high-spin complexes of iron(II)[11,12] and the d^8 configuration in systems with high-spin and low-spin states, for example, in Lifshitz salts[13,14], metal dicyclopentadienides[15], and many tetrahedral halogenocomplexes of Series I transition metals. The development of theoretical postulates was followed by the syntheses of new complexes[16-20]. Since then the ligand field theory has been constantly used for a preliminary interpretation of the results of synthetic and spectroscopic studies by the Rome school. Furthermore, two other fields of theoretical research are being developed: the improvement of the models of the ligand field theory and attempts at a complete description of coordination compounds with the aid of the molecular orbital method.

Among the early studies, an interesting investigation was carried out—namely a detailed analysis of the magnetic susceptibility of d^2 systems[21]. This investigation was followed by an extensive review of the applications of the ligand field theory to the interpretation of the structures and spectra of complexes with a coordination number of five, published in 1968.[22] Subsequently a series of coordination compounds were synthesised and the spectra and structures of their single crystals were investigated: (see below). Numerous studies were performed on the electronic spectra of single crystals, in which the potential possibilities of the ligand field theory for the interpretation of the spectra were used more fully. They will be examined in detail in the section devoted to electronic spectroscopy. The angular overlap method, devised as a development and a revised version of the ligand field theory, was used in certain cases. This model proved to be suitable for the description of the ligand field spectra of the square-pyramidal complex $Fedtc_2Cl_2$ [23] and certain high-spin adducts of the square planar nickel(II) complex $Nidtp_2py_2$.[24] (Here and henceforth dtc = dithiocarbamate, dtp = dithiophosphate, and py = pyridine.)

Calculations on coordination compounds by the molecular orbital method were proposed at the beginning of the 1960'S as an alternative to the ligand field model (the limitations of which are now more clearly seen; its advantages for approximate estimates have also been established). A large number of more or less complex new versions of the molecular orbital method immediately arose and, although none of them can be used as yet without difficulty, they have been extremely valuable.

Theoretical studies of this kind aroused the interest of the Rome school. The problem of such studies was formulated in 1967 at the Symposium on Theoretical Inorganic Chemistry organised by the Peruggia group[25]. After that, certain models for semiempirical calculations by the molecular orbital method, for example, the "full overlap"[26], "zero differential overlap", and analogous methods[27], were developed at the Rome school and tested in practice. Particular attention in the course of this research was devoted to allowance for the effect of open shells (using the Roothaan operator technique).

Despite this, certain calculations on model molecules, such as $[TiF_6^{3-}]$, showed that semiempirical methods of this kind suffer from serious disadvantages. They are associated with difficulties in the parametrisation of empirical quantities. One can now assume that the most promising are the onn-empirical (*ab initio*) computational methods as well as simple semiempirical methods, which, although fairly approximate, are simple to use. As an example, one may quote the improvement of the Wolfsberg–Helmholtz model based on the extensive employment of the Mulliken approximation for the estimation of the contribution of each molecular integral. This model has been used successfully for a number of sulphur-containing complexes, for example $Nidtp_2$ and $Nidtc_2$.[28] As regards the intensification of attempts at the improvement of this method, one may also consider the procedure developed by Fencke where, instead of simple adjustment for self-consistency or the self-consistency of atomic charges, the requirement of the Hartree–Fock SCF is introduced and (or) one uses as a basis for molecular orbital calculations the atomic orbitals obtained by adjustment for self-consistency under the condition of perturbation of the ligand field in the complex investigated, and not the atomic orbitals of free atoms or ions[29].

IV. SYNTHESES

This section deals with the studies in the last decade which have been devoted mainly to complexes containing chalcogenide ligands. The interest in these complexes, where sulphur or selenium serve as donors, arose because of the wide variety of the electronic structures and stereochemical rearrangements and the possibility of comparing them with donor ligands containing oxygen. Thus in the case of sulphur we have a complete set of ligands: a weak field ligand and at the same time a strong π donor S^{2-}, chelating anions of the type dtc^- (R_2NCS_2), dtp^- (R_2PS_2), or dithiocarboxylates ($R-CS_2^-$) (the π-donor and spectrochemical properties of which are extremely different and depend to a large extent on the nature of R), simple neutral thioesters (R_2S), conjugated neutral ligands such as thiourea ($R'R''N-CS-NR'''R''''$) or thiocarbamate esters ($R'OCS-NR''R'''$), and, finally highly conjugated dithiolates.

A spectrochemical comparison of S^{2-}, Se^{2-}, and Te^{2-} by examining the spectra of tetrahedrally coordinated cobalt(II), introduced into the lattices of compounds of the type ZnY or CdY (Y = S, Se, or Te), proved possible for the first group of chalcogenide ligands[30]. The principal studies on chelating dithio-anions were carried out for dithiophosphate complexes. In particular, studies were made on the spectra of nickel(II) dithiophosphates (R = C_6H_5 or C_2H_5O) and their high-spin pseudo-octahedral adducts with nitrogen-containing bases and their X-ray diffraction analysis was carried out[31-34].

The addition of primary aliphatic amines to $Nidtp_2$ takes place in two stages via the formation of a five-coordinated high-spin intermediate, the spectra and reversible formation reactions of which have been studied in detail[35,36]. Other five-coordinated $Nidtp_2$ adducts have been studied by the method of the polarised spectra of single crystals[37]. The same method has been used to compare the properties of a number of phosphorus(III) compounds—dithiophosphates ($Mdtp_3$ or $Mept_3$) dissolved in $Indtp_3$ matrices containing the corresponding dithiocarbamates (In, M)dtc_3.[38] The vanadium(III) compound $Vdtp_3$, synthesised for the first time, is of special interest[39,40]. The reactions of dithiophosphate complexes with bidentate phosphorus and arsenic bases have been investigated[41,43]. As regards dithiocarbamates and related compounds, apart from a few early data on their X-ray diffraction analysis[43-45], systematic studies have been made on the analogous diselenocarbamates $Mdsec_2$, where dsec = $(C_2H_5)_2NCSe_2^-$. These compounds are largely similar to dithiocarbamates, but, in estimating their spectrochemical parameters, it is possible to make interesting quantitative comparisons of their properties.

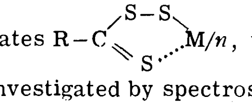
In parallel with the syntheses and spectroscopic studies[46,47], X-ray diffraction studies have also been made on copper(II),[48] nickel(II),[48,49] and zinc(II)[48] complexes. An analogous comparative study of sulphur and selenium compounds has been made for xanthates: several new metal diselenoxanthates $(ROCSe_2)_nM$ were synthesised and studied spectroscopically[50], but they proved to be less stable and less suitable for investigation than diselenocarbamates and diselenophosphates.

From the standpoint of their structures, the dithiocarbazinates ($R_1R_2N-NR_3-CS_2^-$ = dtcz) resemble dithiocarbamates, but they exhibit a greater variety of coordination stereochemistry, since they can behave as bidentate S,S- or S,N-ligands. This depends on several factors, such as the nature of the metal ion, the nature of the substituents influencing the basicity of the nitrogen atoms, and steric conditions. For example, the compounds $Nidtcz_2$ are low-spin square complexes usually forming N,S-chelates in the presence of aliphatic substituents or without substituents and S,S-chelates in the presence of aromatic substituents[51,52]. The complexes of bivalent palladium and copper exhibit similar properties, while zinc shows a greater tendency to form pseudotetrahedral S,S-chelates[53]. The pseudo-octahedral chromium(III) and cobalt(III) complexes can form either S,S- or S,N-chelates[54].

Nickel(II) complexes have been most thoroughly investigated: X-ray diffraction[55,56] and NMR studies[57,58] made it possible to elucidate their coordination stereochemistry and the conformations of the added ligands. These complexes are exceptionally reactive. They undergo deprotonation[59] and alkylation[60] very readily, form labile adducts with oxygen[61], and undergo an unusual cleavage of the N–N bond with formation of the corresponding dithiocarbamates[62].

The dithiocarbazinate esters $R_1R_2N-NR_3-CSSCH_3$ are also effective ligands, forming in the deprotonated form square inner complexes and 1 : 3 pseudo-octahedral complexes with nickel(II).[63] A number of organic reactions of these esters have been studied[63]. Systematic investigations of the corresponding thiocarbazates $R_1R_2N-NR_3-COS^-$ are being prosecuted at the present time[64] and their results will make possible numerous comparison with other compounds, including the hydrazinecarboxylate complexes $(H_2N-NH-COO)_nM$ already known in the literature[65-67].

Studies on the complexes of simple dithiocarboxylic acids R–CSSH or LH (R = alkyl or aryl) are being most vigorously prosecuted; such acids give rise to the simplest possible dithio-anions, but until 1968 they were scarcely used as ligands. Systematic studies, begun in Peruggia, showed that these ligands behave fairly strangely. Thus, although they form inner complexes with the usual stereochemistry (pseudo-octahedral $M^{III}L_3$, square $M^{II}L_2$), a greater degree of mixing of the ligand and metal orbitals (possibly associated with the low electronegativity of R compared with that of R_2N^-, RO^-, etc. in other dithio-anions) is more characteristic of their electronic structure. This is clearly seen, for example, in the electronic spectra, which frequently differ from the usual spectra corresponding to models of the ligand field theory[68]. It has been observed that low-spin nickel(II) complexes[68,69] are not monomeric but form weakly bound trimers Ni_3dtb_6†,[70,71] bridged dimers of the type Ni_2dtpa_4,[31,72] or axial dimers Ni_2dtpv_4,[69,73] or even more complex trinuclear structures of the kind found for dithioacetate[74]. Structures of the type of bridged dimers have also been observed for complexes of monothiobenzoates Ni_2mtb_4. .EtOH (pseudo-octahedral coordination of metal atoms)[75] and Co_2mtb (tetrahedral coordination of the metal)[76], while chromium gives rise to the monomer $Crmtb_3$.[77] Complexes of dithiocarboxylates are also remarkable due to the fact that they are readily transformed into complexes of perthiocarboxylates



$R-C\overset{S-S}{\underset{S}{}}M/n$, which are also being vigorously investigated by spectroscopic[78] and X-ray diffraction[79] methods. Complexes of thiourea with *N*,*N'*-substituted ligands RHN–CS–NHR′, in the case where they exist with the most preferred stereochemistry [for example octahedral stereochemistry for chromium(III)[80] or pseudotetrahedral stereochemistry for cobalt(II) and zinc[81-83]], and when there exist numerous coordination forms, possibly depending on the nature of the substituents R and R′, have been investigated in particular detail. Thus thiourea forms 1 : 4 complexes with palladium(II) and platinum(II), which do not have a simple square structure but are five-coordinated compounds $[ML_4X]^+$ (M = Pd or Pt, L = substituted thioureas, X = halogen or ClO_4) by virtue of the π-acceptor properties of the ligands[84]. On the other hand, in the presence of a molar deficiency of L or an excess of X^-, the complexes ML_2X_2 are formed[84-86]; their formation is also possible in the case of a complex equilibrium.

N,*N'*-Disubstituted selenoureas RHN–CSe–NHR′ behave in relation to palladium(II) and platinum(II) like their sulphur-containing analogues, giving rise to complexes with the same structures and stabilities, let alone the shifts in the spectra[84,87].

Thiocarbamate esters have also been studied, although they exhibit an extremely weak affinity for d^8 metal ions. Their coordination number does not usually exceed two and they are bound, whenever possible, not to the C=S group but to other electron-donating groups, for example the allyl group in PdL_aCl_2 ($L_a = CH_2 = CH-CH_2-NH-CS-OCH_3$) or the deprotonated nitrogen atom in PdL_2'' ($L'' = C_5H_5N^- - CS-OCH_3$).[88-90]

Although the complex-forming properties of thiourea in relation to nickel(II) had been known earlier, they were studied in detail by the present author. Nickel(II) complexes of *N*,*N'*-substituted thio- and seleno-ureas were investigated, which yielded evidence for the existence of different coordination forms and stability series. These series include[91-93] the octahedral chromophores $[NiS_6]$ in certain compounds of the NiL_6X_2 (X = Cl, Br, or I) series and in certain crystalline solid $NiL_6(ClO_4)_2$ specimens, tetragonal chromophores $[NiS_4...X_2]$ in solid NiL_4X_2 specimens, which are in certain cases characterised by a singlet–triplet equilibrium in the ground state, pseudotetrahedral $[NiL_2X_2]$ groups, which exist in the solid form only for fairly bulky ligands but are protonated much more readily in solution, and square $[NiS_4]$ groups, for example,

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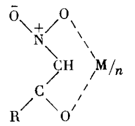
† Here and henceforth dtb = dithiobenzoate and dtpa = dithiophenylacetate.

in thiourea perchlorates (they also formed very readily with selenoureas[94]). Later we began to study complexes of polydentate ureas such as $H_2N-(CH_2)n-NH-CS-NHR$ and $RHN-CS-NH-(CH_2)n-NH-CS-NHR$.[95,96]

Yet another class of ligands, which has been studied in detail in the Rome laboratory, are the α-nitro-ketones $R-CO-CH_2-NO_2$ (mainly $C_6H_5-CO-CH_2-NO_2$) which give rise to chelate rings



analogous to the chelates formed by β-diketones. The greatest number of studies have been devoted to the copper complexes CuL_2 and their five- and six-coordinated adducts[97-100], for which interesting instances of conformational isomerism may be observed. Nickel(II), cobalt(II), and other transition metal complexes have also been investigated[101-104]. Unusual ligand cleavage reactions have been discovered for platinum and gold nitroketonates[105]. The properties of organic nitro-compounds as ligands are always of interest and studies on *gem*-dinitro-compounds $RCH(NO_2)_2$ have been carried out in this connection[106].

The behaviour of hydrazine as a ligand is also of interest, because this compound is a bidentate donor but does not exhibit a capacity for chelate formation. This is evident from the analysis of the spectra and structures of certain nickel(II) complexes with hydrazine and mixed ligands[107-109]. Further synthetic, structural, and spectroscopic investigations dealt with rhenium[110], titanium(II),[111] silver(II),[112] niobium(V),[113] molybdenum(III), and molybdenum(V)[114,115] complexes and transition metal complexes of phthalocyanines (known to exhibit a quasi-reversible NO absorption)[116-118].

In this section we shall also mention studies devoted to complexes of quaternary diphosphine bases and related ligands[119-121] as well as studies on equilibria in solution. Although these investigations have not been part of the main field of research of the Rome school and have not been carried out systematically, they were performed to explain the properties of the less stable compounds. Apart from the early investigations of the copper(II) complexes of aliphatic diamines with long chains[122], 1 : 1 and 1 : 2 paramagnetic adducts of the square $[NiS_4]$ complexes of amines, for example, $Nidtp_2$, have also been studied[26,35]. The stability constants of zinc(II) and cadmium tartrates and citrates in water[123], of cobalt(II) complexes of halogenophosphines in organic solvents[124,125], and of mercury(II) halides in acetonitrile[126] were investigated.

V. KINETICS AND MECHANISMS OF REACTIONS

The study of the reactivities of coordination compounds has been of continued interest at the Chemical Institute of Rome University. Attempts were made to elucidate the mechanisms of substitution in octahedral cobalt(II), rhodium(III), and iridium(III) amino-complexes. Most attention has been devoted to the behaviour of monodentate ligands—carboxylates—in hydration reactions and (or) alkaline hydrolysis in order to establish analogies between these compounds and organic esters[127-133]. Whenever possible, the kinetic data were analysed by plotting linear free energy relations in order to estimate the influence of the geometrical and electronic structures on the kinetics.

In order to discover whether the metal—oxygen or the carbon—oxygen bond is ruptured, experiments using ^{18}O were performed in the most interesting cases. It was found that in neutral or alkaline media hydration proceeds mainly via a dissociative mechanism with rupture of the metal—oxygen bond (acid catalysis takes place at low pH values). The alkaline hydrolysis proceeds either via an S_N1CB mechanism, which is typical of octahedral amino-complexes, or via a $B_{AC}2$ mechanism which is typical of organic esters. In addition, a third reaction pathway, which gives a second order dependence on OH^- and involves the dissociation of the carbon—oxygen bond, was discovered. This mechanism has no analogies in the hydrolysis of esters.

Water exchange reactions were investigated for $[Rh(NH_3)_5(H_2O)]^{3+}$ and $[Ir(NH_3)_5(H_2O)]^{3+}$ and a comparison was made with anation reactions in order to elucidate the role of the interacting groups[134-137]. It was found that, in contrast to the analogous cobalt(III) compounds, the reactions of heavier d^6 metals have an appreciably associative mechanism. This conclusion, supported by modern studies designed to determine the activation volumes in the exchange involving water[138], was unexpected, because numerous kinetic data accumulated for cobalt(III) complexes led to the conclusion that the main reaction pathway for all octahedral complexes involves a dissociative mechanism.

A study was made of the role of the leaving groups in substitution reactions involving certain monoacidic octahedral cobalt(III) and chromium(III) complexes. A linear relation was discovered between the free energies derived from the aquation constants and the values of K_a for the conjugate acids forming part of the ligand[139]. Reactions of the nitrate ion are anomalously rapid from this standpoint, although experiments with ^{18}O showed that its substitution by water proceeds via the dissociation of the metal—oxygen bond[140]. The properties of the nitrate ion as the leaving group have been the subject of special studies[141]. In the series of compounds nitratopentaminecobalt(III), nitratopentaminerhodium(III), and nitratopentamineiridium(III), the NO_3^- anion undergoes alkaline hydrolysis via the usual coupling mechanism, possibly with nucleophilic insertion of a water molecule in the case of heavier metals (S_N2CB). The entropy data show that the freedom of rotation, of which the anion is capable in the transition state, tends to diminish in the sequence $Co > Rh > Ir$.

The series of studies on the reaction mechanisms includes also research into substitution in uncharged ruthenium(II) complexes in non-aqueous solvents[142,143]; kinetic data indicate the formation of five-coordinated intermediates. A study was also made of the hydrolysis and *cis*-*trans* isomerisation in anionic aquo-complexes of ruthenium(IV), containing bidentate ligands (carboxylates)[144]. It appears that the isomerisation mechanism in these instances changes from dissociation at one end of the molecule to dissociation in water with increase of the number of atoms in the chelate ring.

Investigation of the properties of metallocenes in order to elucidate the nature and the site of the interaction of protonating agents with these molecules constitutes a relatively new field[145,146]. The important role of the cyclopentadienyl ring as the basic centre of the molecule was observed[147]. Further studies were devoted to the hydrogen—deuterium exchange in various protic media[148]. The stability constants of certain ferrocenyl carbonium ions were determined and were used to estimate the electron-donating properties of ferrocenyls.

VI. ELECTRONIC SPECTROSCOPY

The study of the electronic absorption spectra of complexes is associated both with theoretical investigations (mainly the assignment of bands in the visible region from the standpoint of the ligand field theory) and with investigations in the field of syntheses, and is part of almost all the publications mentioned in previous sections. Studies devoted to the interpretation of the electronic spectra of coordination compounds, obtained for specimens in the form of single crystals using polarised light, are of special interest for spectroscopy. This field is being developed by the Rome laboratory simultaneously with crystallographic X-ray diffraction investigations. These research techniques make it possible to employ at a deeper level the interpretative possibilities of the ligand field theory with the aid of rigorous selection rules and are widely used in the modern research by the Rome school. The following systems have been investigated: $[CuCl_4]^{2-}$ chromophores with pseudotetrahedral[149] and square planar [150] structures; square $[NiS_4]$ chromophores[151]; certain types of trigonal octahedral complexes of tervalent transition metals with bidentate sulphur-containing ligands[38-40]; the dinuclear complex $Nidtpa_4$ (where dtpa = dithiophenylacetate)[72]; pseudotetrahedral cobalt(II) complexes with various *s* and *p* donors[152]; the $[MnCl_5]^{2-}$ ion[153]; eight-coordinated tetranitrato-complexes[154]; and certain other transition metal complexes, mainly those of nickel and copper.

Another spectroscopic method, which has been developed particularly vigorously in recent years in Rome and Peruggia, involves the study of the luminescence spectra of inorganic chromophores. Both fluorescence and phosphorescence spectra yield important information for the determination of the positions and the identification of excited electronic levels and thus supplement data obtained with the aid of absorption data. Furthermore, luminescence spectra make it possible to study phenomena involving excitation via structural energy transfer and the reactivities of metal complexes. Despite its considerable advantages, emission spectroscopy is used much more rarely than absorption spectroscopy, possibly because of considerable technical difficulties and appreciable limitations in its applicability. Nevertheless this method has attracted the attention of the Rome school, which has been reflected in papers devoted to the general discussion of emission spectra[155,156], the consideration of luminescence spectra of chromium(III) complexes of sulphur-containing ligands[157] and ethylenediaminetetra-acetic acid[158], platinum(II),[159,160] platinum(IV),[161] and manganese(II) [162] complexes, as well as certain instances of energy transfer to the centres responsible for luminescence or between these centres[163].

Mention should be made in this section also of research in the photochemistry of coordination compounds [mainly chromium and chromium(III) complexes], which is directly related to the study of luminescence spectra. The formation of the same preceding state—an excited ligand field or charge-transfer state—is necessary for both processes—a photochemical reaction or luminescence. As a result, the data obtained with the aid of the two methods supplement each other and thus make it possible to describe more accurately the excited states of metal complexes. The first studies were performed jointly with two leading groups in the field of inorganic photochemisty—those of Schläfer (emeritus Professor at Frankfurt)[164] and Prof. Adamson in Los Angeles[165,166]. These studies initiated original research into the mechanisms of photochemical substitution reactions involving certain chromium(III) complexes[167,168], particularly the *trans*-disubstituted complexes $[CrA_4XY]$, in which isomerisation and (or) substitution takes place[169,170]. Among other studies[171,172], those on the mechanisms of energy transfer from certain sensitisers in reactions of chromium(III) complexes are of special interest[173,174].

VII. VIBRATIONAL SPECTROSCOPY

The method is used mainly as an auxiliary procedure in the determination of structures or in order to test theories of bonding in coordination compounds. A number of early studies were devoted to the influence of the ligand field on the bond vibration frequencies in the molecule of the complex and in the ligands. In order to account for the vibration frequency shift in coordinated water molecules[175,176] and NH_4^+,[177,178] and BH_4^- ions in crystals[179], the method of perturbation theory was used. The normal coordinates have been analysed for certain cyano-complexes[180], carbonyls[180], and other coordination compounds.

Later, interest was concentrated on empirical problems associated with developing synthetic studies. For example, infrared spectroscopic data for nitroketone[181,182], dithio- and perthio-carboxylate[183-185], and a number of other complexes[186,187] have been published together with descriptions of the syntheses of the complexes and their other structural properties. In particular, investigations on nitroketone complexes began with the study of the infrared spectra of free nitroacetone and nitroacetophenone, the band assignments in the spectra being confirmed by the isotopic shifts for certain deuterated analogues[188]. Among metal complexes, copper(II) bis(nitroacetophenonate) has been most thoroughly investigated, because the simple structure of its crystal lattice permits a more accurate calculation[189]. In further investigations of nitroacetophenonates of other bivalent transition metals, copper(II) bisnitroacetonate, and certain univalent metal dinitroacetonates, satisfactory evidence was obtained for the delocalisation of the charge over the chelate rings and the influence of substituents[190].

The dithiobenzoates ($C_6H_5-CSS^- = dtb^-$), dithiophenylacetates ($C_6H_5-CH_2-CSS^- = dtpa^-$), dithioacetates ($H_3C-CSS^- = dtac^-$), and perthiobenzoates ($C_6H_5-CS_2S^- = dtbD^-$) of certain bivalent and tervalent transition metals have been particularly thoroughly investigated. These investigations were associated with the problem of the assignment of the intense stretching vibration bands due to C–S, S–S, and other bonds in the chelate rings, for which there are contradictory literature data. Final conclusions were reached in experiments with deuteration, the observation of splittings in the spectra of crystals, and in certain instances with the aid of polarised infrared spectra of thin films[184,185].

VIII. ELECTROCHEMISTRY

As in other Italian universities, the scientists at Rome showed a deep interest in electrochemistry even before the war, particularly in polarographic studies on complexes[1,191]. Recently, the polarography of coordination compounds in an aqueous medium has been used to study the kinetics of the decomposition of $[Mn(C_2O_4)_3]^{3-}$ [192] and of complex formation in the system comprising copper(II) and polydentate amines[193-195] and in the study of the behaviour of certain organic ligands such as heterocyclic nitrogen-containing bases[196,197] or dithiocarboxylates[198] at electrodes and of the polarographic properties of molybdenum(V)[199] and molybdenum(III).[200] However, polarography in aqueous solutions is at present being displaced by other methods, which are more powerful and are more widely applicable in the chemistry of coordination compounds: on the one hand, polarography in non-aqueous solvents and, on the other, pulsed electrolysis, particularly chronopotentiometry.

Polarography in non-aqueous solvents is used to study compounds which are insoluble or undergo decomposition in water. Furthermore, it is used in investigations involving protic and aprotic systems more or less similar to water. As regards water-insoluble compounds, aromatic disulphide–mercaptan systems have been studied in benzene–methanol mixtures, while related ligands of the type of dithiocarboxylates have been studied in water, acetonitrile (AN), and propylene carbonate (PC).[198] They were reduced to polymeric thioaldehydes, which, however, undergo certain side reactions.

Among metal complexes which do not dissolve in water without decomposition, the sandwich aromatic complexes of chromium have been studied in benzene–methanol mixtures, where the Cr^0/Cr^+ redox process approaches closely polarographic reversibility and is sensitive to the influence of substituents in aromatic ligands[202-205]. The tetrahedral transition metal halide complexes $[MX_4]^{2-}$ are fully hydrolysed in water, but can be investigated either in dimethylformamide[206,207] or in acetonitrile[208]. The properties of copper(II) complexes, which react with mercury at the electrode but exhibit normal properties at a platinum microelectrode, are of special interest[207,208].

In studies on polarography, continued at the present time and associated with synthetic research, the most suitable solvents proved to be acetonitrile and propylene carbonate. Dithiocarboxylate ligands and complexes have been investigated in propylene carbonate[198], while the properties of halogenomercury complexes[209] and mixed halogenophosphinecobalt(II) complexes[210,211] have been investigated in acetonitrile. A particular advantage of acetonitrile as a solvent is that it can be used simultaneously in both polarographic and potentiometric studies (the latter with Mo or W indicator electrodes), as well as spectrophotometric measurements. The joint use of the three methods enumerated makes it possible to describe quantitatively the complex equilibrium established in the systems mentioned above, incorporating mercury and cobalt complexes[209-212].

The limited applicability of the usual polarography led investigators to employ in many instances other electrochemical methods in order to investigate electrode processes involving metal complexes. The most successful attempt was that undertaken at the Rome school to employ pulsed d.c. electrolysis or transitometry. Catalytic reduction reactions of metal complexes have been studied both experimentally {for example in the $[Ni(CN)_4]^{2-}$ system}[213] and theoretically. For this purpose, a relation was established between the transfer time and the kinetic parameters for certain complex catalytic systems[214,215] and electrolytic reduction was studied after reversing the current[216].

The dependence of the current density on the concentrations of ligands and complexes has been determined with the aid of another important parameter, measured in pulsed d.c. electrolysis (the initial reduction potential) by recording the voltage–current characteristics for a non-polarised current. The parameter is used to obtain information about the mechanisms of the electrode reactions of certain metal complexes[217], for example, the electrode reactions of cadmium(II) and zinc[218], nickel(II) and copper(II),[219,220] and iron(II) and iron(III),[221] and especially in the study of ligand and (or) proton association or dissociation reactions in the bulk of the solution before discharge at the electrode. The method suffers from limitations, particularly in the case of very high rates of charge transfer at the electrode. Despite this, it has been used in many studies and has made it possible to identify a number of interesting electrochemically active complexes, frequently different from the compounds formed at equilibrium in solution[218-221].

IX. OTHER METHODS

The magnetic resonance methods have usually been employed as auxiliary procedures in relation to the more common methods, most of which have already been described in preceding sections. From the standpoint of microwave spectroscopy, studies on nuclear quadrupole resonance (NQR) of the halogens in halogeno-complexes, for example NQR of chlorine in certain crystalline tetrachloroureas, are of special interest[222,223].

Proton magnetic resonance has been used to confirm conclusions concerning the stereochemistry and reactivity of certain sulphur-containing complexes and the corresponding ligands. Dithio-, perthio-, and mixed dithioperthio-complexes of transition metals may be identified with the aid of NMR and their interconversions may be followed[224]. The preferred conformations of certain substituted thioureas, both in the free state and as part of cobalt and zinc complexes, have been determined, which involved calculations on theoretical models of the corresponding structures[225-227]. The knowledge of conformation assisted in its turn in the elucidation of the contribution and role of hydrogen bonds, both intermolecular and intramolecular, which may be formed in metal–urea complexes in large numbers[226,227]. The conclusions reached have been confirmed by infrared spectroscopic data[82] and by X-ray diffraction[83,228]. In particular, it was shown that, for certain pseudotetrahedral dichlorobis(substituted urea)–zinc and –cobalt(II) complexes, the formation of intermolecular hydrogen bonds leads to chain polymerisation and that the resulting structures resemble to some extent the regular arrangements of polypeptide chains[83,228].

Photoelectron spectroscopy has been used on an increasing scale in research by the Rome school in recent years. The possibility of employing X-ray electronic spectroscopy in inorganic chemistry is still controversial as regards the validity of the measured ionisation energies the role of the effects of the solid phase in the determination of corrections to the results, and the factors influencing the true ionisation energy. Despite this, there is no doubt that the method has considerable potential possibilities for both analytical and structural research.

In the present author's studies attention was concentrated on certain aspects of the chemistry of complexes. X-Ray electronic spectroscopy makes it possible (to a greater extent than other methods) to determine the degrees of oxidation of two elements in certain rhodium–molybdenum heteropolyacids[229]. As regards molecular systems containing atoms in a common oxidation state, we investigated certain nickel(II) complexes of dithiocarbazin acid $H_2N-NH-CSSH$ and its derivatives as well as the corresponding free ligands. These are ambident ligands i.e. contain several potential electron donors. Since the degree of their oxidation is known, the change in electron binding energy yields information about the overall atomic charge—a quantity which is of fundamental importance for theoretical coordination chemistry, but is rarely susceptible to direct experimental determination. We were thus able to distinguish electron-donating atoms involved and not involved in complex formation and to obtain a schematic distribution of atomic charges along the complex of the complex[230]. Chromium(II) complexes, metal nitrosyls (particularly rhenium nitrosyls), and platinum acetylides have also been investigated by X-ray electronic spectroscopy.

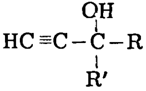
Photoelectron spectroscopy with excitation by ultraviolet light yields more detailed information about the ionisation energies of valence orbitals. A significant limitation of this method is the requirement that the molecules investigated must be in vapour phase. Despite this limitation, the method has found extensive applications in coordination chemistry, where it can yield more extensive and more detailed information about the sequence of energies and the nature of the valence orbitals than the usual methods. The systems investigated in Rome include fluorinated sulphur-containing complexes, mainly perfluorodithiocarboxylates and the corresponding ligands [231], difluorodithiophosphates[232], and particularly thio- and dithio-derivatives of metal β-diketonates, such as nickel(II) bis(dithioacetylacetonate) and similar volatile nickel(II), cobalt(II), copper(II), and zinc complexes[233]. The existence of *d* orbitals adjoining or mixed with ligand orbitals, which differs from the traditional idea of clearly defined, separate, and partly filled electron shells in transition metal complexes, has been observed in these compounds.

X. APPLIED RESEARCH

Although applied research in the Rome school has not been of the type of systematic actively developing investigations, studies have been made on certain systems which are of potential or real applied interest, mainly catalytically active complexes and models for organic catalysis.

Studies of this kind were begun at the end of the 1950's, in collaboration with research workers of Natta's group in Milan in connection with the extensive applications of the Ziegler–Natta catalysts for the polymerisation of olefins. The first attempts were directed towards the elucidation of the structures of the active products of the reactions between transition metal halides (or acetylacetonates) and aluminium alkyls. For example, the formation of labile Cr(O) compounds was established in the reaction between $Cr(acac)_3$ and $AlEt_3$.[234,235] Subsequent investigations were devoted to the determination of the catalytic activities of certain Ziegler–Natta catalysts of the polymerisation reactions of acetylenic hydrocarbons[236-240]. It was found that monosubstituted acetylenes are converted into a mixture of symmetrical and asymmetric trisubstituted benzene derivatives. The yield of aromatic trimers usually depended on the catalyst : cocatalyst ratio. However, when different monomers were employed, the maximum yield did not correspond to the same catalyst : cocatalyst ratio. Linear polymers were also sometimes investigated.

Studies have been likewise carried out on other catalytic systems in order to find simpler reaction conditions. In fact, when catalysts of the Ziegler–Natta type are used, oxygen and water must be completely absent from the system. It was found that triphenylphosphinenickel complexes act as polymerising agents even when the reaction is carried out in solvents containing water and in air[241,242]. In the course of these investigations it was observed that the complex $(n\text{-}Bu_3P)_2NiBr_2$ is a very active catalyst for the trimerisation of α-hydroxyacetylenes having the general formula $HC{\equiv}C-\overset{\displaystyle OH}{\underset{\displaystyle R'}{C}}-R$, pure 1,3,5-trisubstituted benzene derivatives being obtained in very high yields. Asymmetric isomers were not found in the reaction mixture[243].



In order to elucidate the role of transition metals in the mechanisms of catalytic reactions, a series of platinum complexes of bis(triphenylphosphines) were synthesised[244,245] and their catalytic activity was investigated in the polymerisation of phenylacetylene and 2-methylbut-3-yn-2-ol [246,247]. In the presence of platinum complexes monosubstituted alkynes were converted into linear polymers. Complexes having the general formula $[(C_6H_5)_3P]_2Pt(C{\equiv}C-R)_2$, containing the monomer linked by a σ bond to the platinum atom, were identified and isolated from the crude reaction mixture. These complexes may in fact be the active intermediates in the polymerisation reaction. There is evidence that the polymer chain grows as a result of the insertion of the monomer molecule in the Pt–C σ bond.

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The Chemistry of 1,5,9-Cyclododecatriene and Syntheses Based on It

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The methods of synthesis and chemical properties of 1,5,9-cyclododecatriene (the butadiene cyclotrimerisation product), which is manufactured on an industrial scale, are examined; syntheses based on this interesting compound have played a major role in the development of organic chemistry of medium and large rings.
The bibliography includes 406 references.

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I. INTRODUCTION

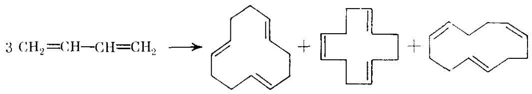
The first studies on cyclododecane and its derivatives were begun in 1926 by Ruzicka and coworkers, but the difficulty of the synthesis of these compounds and of their isolation in a pure form hindered the development of their chemistry.

In 1954, Reed reported for the first time[1] the synthesis of a cyclic butadiene trimer in the presence of bis(triphenylphosphine)nickel dicarbonyl, but it was not until Wilke's study[2] of the cyclotrimerisation of butadiene in the presence of organometallic complex catalysts that 1,5,9-cyclododecatriene (1,5,9-CDT) became readily available and vigorous development of the chemistry of this compound and its industrial use were initiated.

cis,trans,trans-1,5,9-CDT is manufactured at present on a large scale in many countries. The following products obtained from 1,5,9-CDT are of major technical importance: ω-dodecalactam—the monomer for the synthesis of nylon-12; decane-1,10-dicarboxylic acid—the monomer for the synthesis of polyamides and polyesters and a substitute of sebacic acid in the synthesis of plasticisers and lubricating oils; 1,12-diaminododecane—the monomer for the synthesis of polyamides; 1,2,5,6,9,10-hexabromocyclododecane, which is used as an additive to polymers in order to render them incombustible; cyclododecanone which is used as the initial compound for the synthesis of valuable perfumes—cyclopentadecanone (exaltone) and the lactone of ω-hydroxypentadecanoic acid (tibetolide).

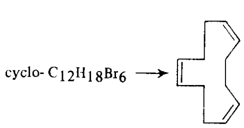
II. SYNTHESIS AND CHEMICAL REACTIONS OF 1,5,9-CYCLODODECATRIENE ISOMERS

It has now been established that the cyclotrimerisation of butadiene to 1,5,9-CDT proceeds in catalytic systems containing the following transition metals as components: titanium, chromium, nickel, and manganese. *trans,trans,trans*-1,5,9-CDT (I), *cis,trans,trans*-1,5,9-CDT (II), and *cis,cis,trans*-1,5,9-CDT (III) have been obtained in the presence of these catalysts; the ratios of the yields of these products depend on the nature of the transition metal, the ligands in the catalytic system, and the reaction conditions:



(I) (II) (III)

The fourth possible isomer—*cis,cis,cis*-1,5,9-CDT (IV)—is not formed in the catalytic trimerisation of butadiene. It has been obtained by the dehydrobromination of hexabromocyclododecane—the product of the addition of three bromine molecules to (I):[3]

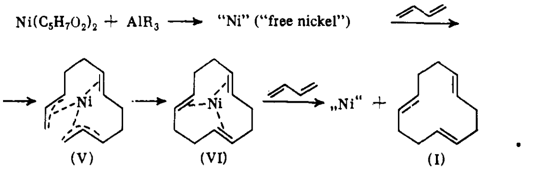


(IV)

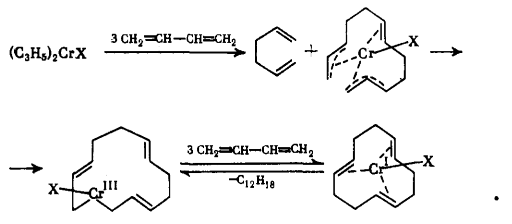
The most effective catalysts for the synthesis of 1,5,9-CDT are systems containing various titanium compounds [$TiCl_4$,[4-20] $TiBr_4$,[21] $Ti(OR)_4$,[22,23] $(RO)_2TiO$,[24] $TiCl_{4-n}(OR)_n$, $TiCl_{4-n}(OCOR)_n$,[25-28] and the complex $C_6H_6.TiCl_2.Al_2Cl_6$ [13,29,30]] in combination with reducing agents such as trialkylaluminium or aluminium alkyl halides, calcium hydride, and dialkylaluminium hydride. The reaction proceeds only in solution in aromatic hydrocarbons with formation of 1,5,9-CDT in 80–90% yield. The 1,5,9-CDT obtained is a mixture of two isomers: 3–4% of (I) and 96–97% of (II). A mixture containing 67% of (I) and 33% of (II) is formed in the catalytic system containing poly(butyl orthotitanate) and $(C_2H_5)_2AlCl$.[31]

Catalytic systems containing chromium and manganese [$(C_5H_7O_2)_2Cr$, CrO_2Cl_2 or $CrO_3 + (C_2H_5)_3Al$,[4,5,12] $CrCl_3 + (iso\text{-}C_4H_9)_3Al$,[10-12,32,33] and $(C_5H_7O_2)_2Mn + (C_2H_5)_3Al$ [34]] lead to a mixture of approximately 60% of (I) and approximately 40% of (II). A mixture consisting of 65–80% of (I), 7–9% of (II), 9–11% of (III), 7–9% of vinylcyclohexene, and 4–6% of 1,5-cyclo-octadiene is formed in the presence of nickel catalysts [$Ni(C_5H_7O_2)_2 + C_2H_5OAl(C_2H_5)_2$,[12,35,36] $NiX_2 + (iso\text{-}C_4H_9)_3Al$,[37] $(cyclo\text{-}octadiene)_2.Ni(O)$ [30,36] and cyclododecatriene.Ni(O) [35]]. The mixture composition varies with reaction temperature.

There have been numerous patents for catalytic systems containing nickel[37,38–43]. The mechanism of the reaction in the presence of nickel catalysts has been established by Wilke and coworkers[33,35,44–46]. It includes the following stages:



When $Ni(C_5H_7O_2)_2$ is reduced by an organoaluminium compound, "free" nickel is formed, which trimerises butadiene to the intermediate π-allyl complex of nickel (V); ring closure of (V) results in the formation of the π-nickel complex (VI). Treatment with butadiene leads to the displacement of 1,5,9-CDT from this complex. Complexes (V) and (VI) have been isolated and their structures have been determined by X-ray diffraction[47,48] and confirmed by certain reactions[31,35,44,45]. When complex (VI) is acted upon by *cis,cis,cis*-1,5,9-CDT (IV), *trans,trans,trans*-1,5,9-cyclododecatriene (I) is displaced from it and the complex (IV).Ni(O) is formed[45]; the latter readily reacts with carbon monoxide to give $Ni(CO)_4$ and compound (IV). A mechanism has been proposed for the trimerisation of butadiene in the presence of chromium catalysts[33] in which the valence state of chromium changes continuously from +1 to +3:



It has been shown[30,49] that in the presence of titanium catalysts the active centre for the trimerisation of butadiene is a complex in which titanium is present in the bivalent state:

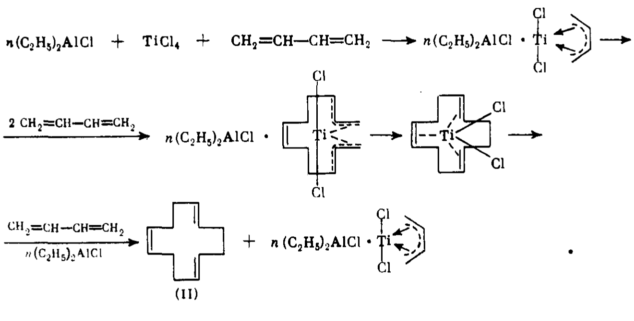


Table 1 presents the best known catalytic systems in the presence of which the trimerisation of butadiene to 1,5,9-CDT isomers takes place with a high yield.

Among the four 1,5,9-CDT isomers, the *trans,trans,trans*-isomer (I)[50] and the *cis,trans,trans*-isomer (II), which are readily obtainable in the presence of the above catalysts, have been studied in greatest detail. The presence of three non-conjugated double bonds in the 1,5,9-CDT molecule makes this system capable of undergoing many reactions. Among them the most interesting are those involving *cis–trans* isomerisation. When (II) is illuminated with ultraviolet light, a mixture of (I) and (III) is formed[51].

Table 1.

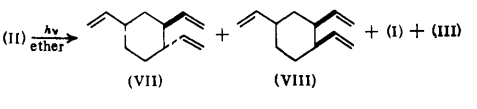
Catalytic systems	Yield of 1,5,9-CDT, %	Isomers formed (the relative percentage contents are indicated in brackets)	Refs.
$TiCl_4 + (C_2H_5)_2AlCl$	91	I (97) + II (3)	8, 9, 10
$TiCl_4 + (C_2H_5)_3Al_2Cl_3$	88	II (98) + I (2)	8, 9, 12
$CrO_2Cl_2 + (C_2H_5)_3Al$	70	I (59) + II (41)	10
$CrCl_3 + (C_2H_5)_3Al$	80	I + II	8
$CrCl_3 + (iso\text{-}C_4H_9)_3Al$	86	I (60) + II (40)	8, 9
$Ni(C_5H_7O_2)_2 + (C_2H_5)_2AlOC_2H_5$	81	I (80) + II (9) + III (11)	10
$NiX_2 + (iso\text{-}C_4H_9)_3Al$	80	I+II	37
$[(C_8H_{12})_2Ni]$	87	I+II	39

Subsequently it was shown that each of the four isomers undergoes cis–trans isomerisation giving rise to the same equilibrium mixture consisting of all four isomers (I), (II), (III), and (IV).[52] It has been established[53] that thermodynamic stability decreases in the sequence (I) > (II) > (III). Data for the photochemical isomerisation of the isomers in benzene are presented in Table 2.

Table 2. Composition of the mixture of 1,5,9-CDT isomers in photochemical isomerisation[53].

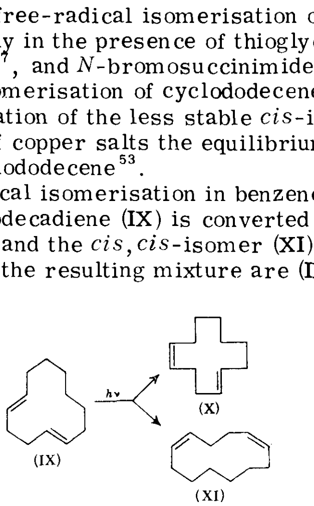
Initial olefin	Irradiation time, h	Proportions of isomers in product, %		
		(I)	(II)	(III)
(I)	17	24	43	33
(II)	17	11	55	34
(III)	100	1	21	78

Table 2 shows that (III) isomerises much more slowly than isomers (I) and (II). The proportions of the isomers also depend on the selected sensitiser. In the presence of aromatic ketones and quinones, isomer (II) predominates in the resulting mixture, while the use of aliphatic ketones leads to isomer (III). Thus the readily available isomer (II) may be easily converted into (I) and (III) on irradiation of a benzene solution containing acetophenone or acetone. After prolonged irradiation of a mixture of (I), (II), and (III), 43% of *trans,trans*-2,6-divinyl-*cis*-bicyclo[3,3,0]octane was obtained together with 1,5,9-CDT isomers[52]. When (II) in an ethereal solution is irradiated, a mixture containing 25% of (I), 29% of (III), and isomeric 1,2,4-trivinylcyclohexanes [12% of (VII) and 1% of (VIII)] is formed[54]:

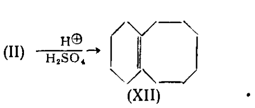


Thermal isomerisation of (II) at 450°C leads only to isomeric 1,2,4-trivinylcyclohexanes[55]. In the presence of toluene-*p*-sulphinic acid a mixture of 80–85% of (I) and 15–20% of (II) is formed from the initial (I)–(III) mixture on heating to 90° C.[53,56] Copper salts are active catalysts of the *cis–trans* isomerisation of the double bonds in (I), (II), and (III).[53] The free-radical isomerisation of (II) to (I) takes place readily in the presence of thioglycolic acid[57], benzoyl peroxide[57], and *N*-bromosuccinimide[57,58]. The photochemical isomerisation of cyclododecenes in benzene leads to the formation of the less stable *cis*-isomer[53]. In the presence of copper salts the equilibrium is also displaced to *cis*-cyclododecene[53].

On photochemical isomerisation in benzene, *trans, trans*-1,5-cyclododecadiene (IX) is converted into the *cis, trans*-isomer (X) and the *cis,cis*-isomer (XI); the ratios of the isomers in the resulting mixture are (IX) : (X) : (XI) = 17 : 55 : 28[59]:

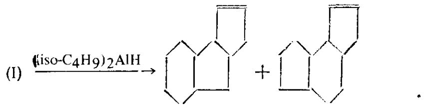


In the presence of acid reagents (II) undergoes intramolecular cyclisation, which leads to products with bicyclic and tricyclic structures. Thus a mixture of hydrocarbons in which $\Delta^{1,6}$-bicyclo[4,6,0]dodecene (XII) predominates, is formed from (II) on treatment with 80% sulphuric acid in the cold[60]:

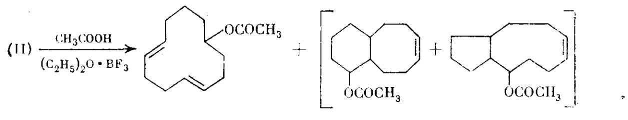


A mixture of acenaphthene and decahydroacenaphthene is formed on heating (II) with polyphosphoric acid[61].

The isomerisation of (I) takes place readily in the presence of (iso-$C_4H_9)_2$.AlH on heating to 200° C, giving an 85% yield of a mixture of tricyclo[6,4,0,$0^{3,7}$]dodec-4-ene and tricyclo[7,3,0,$0^{3,7}$]dodec-4-ene[62]:

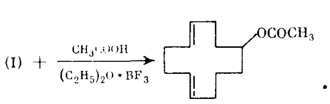


Bicyclic products were formed after the addition of acetic acid and hydrogen chloride to (II)[63]:

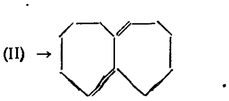


The reaction apparently proceeds both at the *cis*-double bond, giving rise to the usual addition products, and at the *trans*-double bond, giving rise to bicyclic products.

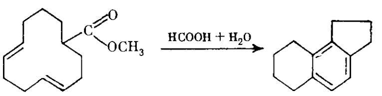
When acetic acid and hydrogen chloride react with (I), only addition products retaining the molecular skeleton are formed[63]:



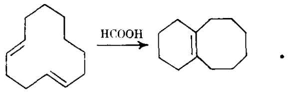
Bicyclo[5,5,0]dodeca-1,7-diene is formed from (II) in the presence of Na/Al_2O_3,[64] $Co_2(CO)_8$,[65] and the lithium derivative of ethylenediamine[66]:



When methyl *trans, trans*-4,8-cyclododecadiene-carboxylate is treated with 90% formic acid, 2,3,6,7,8,9-hexahydro-1H-benz[*e*]indene is produced[67].

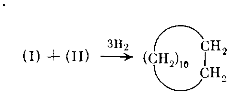


trans, trans-1,5-cyclododecadiene gives rise to bicyclo-[6,4,0]dodecene[67]:



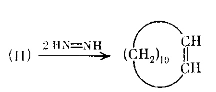
III. SYNTHESES BASED ON *cis, trans, trans*- AND *trans, trans, trans*-1,5,9-CYCLODODECATRIENES

In this section of the review we shall consider the reactions of the most readily available 1,5,9-CDT isomers—the *trans, trans, trans*-isomer (I) and the *cis, trans, trans*-isomer (II). The majority of studies on the hydrogenation of 1,5,9-CDT in cyclododecane are described in the patent literature. The two isomers (I) and (II) are quantitatively hydrogenated in the presence of platinum, palladium, and Raney nickel[68-70]:



In order to obtain large amounts of cyclododecane, (I) and (II) are hydrogenated at elevated temperatures in the presence of Ni/Al_2O_3 or Ni/Cr_2O_3.[5,68-72] Nickel, cobalt, and copper salts deposited on SiO_2 or Al_2O_3 in the presence of NaF are effective catalysts of the reduction[73,74]. The rates of hydrogenation of the two isomers are virtually the same. In the presence of these catalysts, all three double bonds are hydrogenated at virtually the same rates and one cannot therefore carry out a selective hydrogenation. When one mole of (II) is hydrogenated with two moles of hydrogen in the presence of palladium, a mixture consisting of cyclododecene, cyclododecadiene, and cyclododecanes is formed[68,75]. The hydrogenation of (I) and (II) to cyclododecane in the presence of homogeneous catalysts has been described in a number of patents: $(Ph_3As)_2(CO)RhCl$ + $AlCl_3$,[76] $Ni(C_5H_7O_2)_2$ + $LiAlH_2(OCHMeC_2H_5)_2$,[77] $Ti(OBu)_4$ + $(C_2H_5)_2AlCl$, and $Cr(C_5H_7O_2)_2$ + $(C_2H_5)_2AlCl$ + $(C_2H_5)_3Al$.[79]

The selective hydrogenation of (I) and (II) to cyclododecene, which gives rise to great possibilities for the synthesis of many products of practical importance, is of considerable interest. It has been shown that, when (II) is acted upon by di-imide, the *trans*-double bonds are reduced initially and *cis*-cyclododecene is formed in a high yield[80,81]:

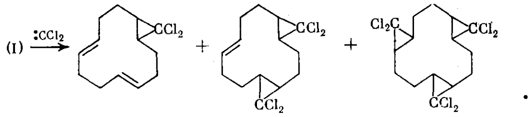


The success of the catalytic hydrogenation of (II) to cyclododecene depends primarily on the nature of the catalyst. The use of relatively inactive heterogeneous catalysts makes it possible to stop the hydrogenation at the stage corresponding to the addition of two moles of hydrogen[82-87]. Studies on a series of catalysts (Rh, Pd, and Ru on Al_2O_3)[88,89] have shown that the hydrogenation of (I) and

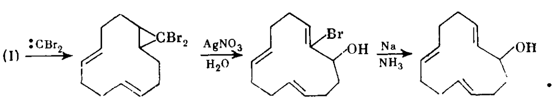
(II) to cyclododecene takes place most selectively in the presence of rhodium. The catalysts can be arranged in the following sequence in terms of decreasing yields of cyclododecene: Ph > Pd > Ru > Pt. The trichlorotripyridinerhodium +$NaBH_4$ catalytic system proved to be the most effective in the hydrogenation (II) to cyclododecene[90]. In the presence of the homogeneous catalyst $[Co(CO)_3.PR_3]_2$[83,84,91] or $(R_3P)_2(CO)_2RuCl_2$[92,93] (II) gives a high yield of a mixture of *cis*- and *trans*-cyclododecenes (96–98%) and in addition 1% of 1,5-cyclododecadiene and 0.5% of cyclododecane are formed. Hydrogenation of (II) in the presence of 7% $PtCl_2$ in a $(C_2H_5)_4NSnCl_2$ melt at 160°C and 100 atm of H_2 leads to 2% of (II), 10% of cyclododecadiene, and 87% of cyclododecene[94].

The addition of halogens and halogenocarbenes, oxidation, hydroboration, and carboxylation are other reactions involving double bonds in (I) and (II). When (I) and (II) are brominated, a mixture of dibromocyclododecadiene, tetrabromocyclododecene, and hexabromocyclododecane is formed[68,95,96]. However, it has been stated in patents[97,98] that, when one mole of (I) is brominated with two moles of Br_2 in the presence of sodium acetate, tetrabromocyclododecene is formed quantitatively. It has been shown[68] that hexabromocyclododecane obtained from (II) has a melting point of 194–195°C, while that obtained from (I) has a melting point of 177–178°C. These bromo-derivatives are different geometrical isomers. On recrystallisation from benzene, the hexabromocyclododecane obtained from (I) gives rise to the clathrate compound $(C_{12}H_{18}Br_6)_2C_6H_6$.[75] Hexabromocyclododecane has found an application as an additive to polymeric materials in order to render them incombustible.

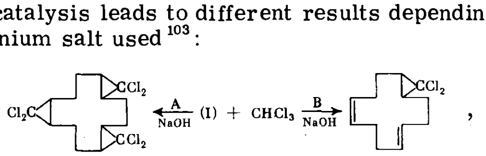
The addition of halogenocarbenes to (I) and (II) has been investigated in detail. The addition of $:CCl_2$ to (II) takes place preferentially at the *trans*-double bond[99]. When $:CHCl$[100] and $:CCl_2$[101] act on (I), a mixture of three products is formed:



Treatment of (I) with $:CBr_2$ gives a high yield of dibromobicyclotridecadiene[102], which on treatment with $AgNO_3$ in water is converted into bromohydroxycyclotridecatriene; on treatment with sodium in liquid ammonia, the latter is converted into hydroxycyclotridecatriene:



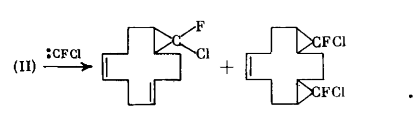
The addition of $:CCl_2$ to (II) under the conditions of phase-transfer catalysis leads to different results depending on the ammonium salt used[103]:



(XIII)

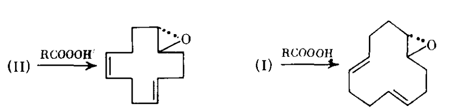
where A = cetyltrimethylammonium bromide and B = trialkyl-β-hydroxyethylammonium bromide. When the diene (XIII) is hydrogenated, the product is 13,13-dichlorobicyclo[10,1,0]tridecane, from which cyclotridecanone was obtained[104]:

The reaction of (II) with :CFCl takes place at the *trans*-double bonds with formation of two addition products[105]:



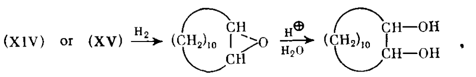
The addition of $:CHOCH_3$ to (I) entails the formation of only *trans*-13-methoxybicyclo[10,1,0]trideca-*trans*,*trans*-4,8-diene, while a mixture of diastereoisomers is formed from (II) under these conditions[106]. The reaction of $:CCl_2$ with *cis*,*trans*-1,5-cyclododecadiene takes place unambiguously, resulting in the formation of *trans*-13,13-dichlorobicyclo[10,1,0]tridec-4-ene(*cis*).[108] A study of the rates of addition of :CHCl,[100] $:CBr_2$,[107] and $:CHOCH_3$[106] to *cis*- and *trans*-cyclododecenes showed that the reaction involving the *trans*-double bond is faster.

The oxidation of (I) and (II) to epoxycyclododecadiene, further transformations of which lead to interesting and valuable products, is preparatively important. The epoxidation of (I) and (II) has been carried out with peracetic, perbenzoic, and perphthalic acids, as well as a mixture of H_2O_2 and CH_3COOH in the presence of a cation-exchange resin[5,11,68,109-114]. In the epoxidation of (II) the *trans*-double bond reacts first with formation of the epoxydiene (XIV)[68]:

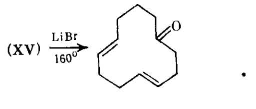


(XIV) (XV)

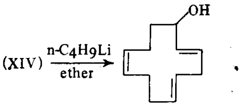
It has been established[112] that monoepoxidation of (II) results in the formation of 92% of the *trans*-epoxide and 7% of the *cis*-epoxide. The epoxidation of (I) yielded the epoxydiene (XV). The oxidation of (I) and (II) by atmospheric oxygen in the presence of boric acid or its esters leads to the formation of epoxycyclododecadiene together with 2,6,10-cyclododecatrienol[115]. The synthesis of 5,6 : 9,10-diepoxycyclododecene, 5,6 : 9,10-diepoxycyclododecane[116], 1,2 : 5,6 : 9,10-triepoxycyclododecane[117], and epoxycyclododecene[118,119] has been described in patents. The opening of the epoxy-rings of these compounds results in the formation of the corresponding diols, tetraols, and hexaols[68,74,120-122]; thus (XIV) and (XV) give rise to the corresponding *trans*-dihydroxycyclododecadienes[68]. The reduction of double bonds in (XIV) and (XV) leads to *trans*-epoxycyclododecane and subsequent opening of the epoxy-ring gives rise to *cis*-1,2-cyclododecanediol[68,123]:



In the presence of catalytic amounts of Group I and II metal halides epoxycyclododecadienes readily isomerise to the corresponding ketones[124,125]:

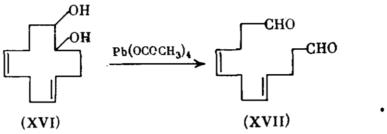


Two isomeric unsaturated ketones with different positions of the keto-group in relation to the C=C double bonds are formed from (XIV).[125] When (XIV) is acted upon by (iso-$C_4H_9)_2AlH$,[126] n-C_4H_9Li, or C_4H_9MgBr [127] isomerisation with formation of unsaturated alcohols takes place:

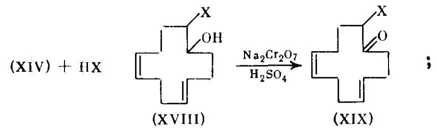


The isomerisation of the epoxide and the formation of cyclododecanone[11,75,110] together with cyclododecanol are observed in the catalytic hydrogenation of (XIV) or (XV) in the presence of nickel catalysts (Raney nickel, Ni/Al_2O_3, Ni/Cr_2O_3) at 120–150°C.

When (II) is oxidised by OsO_4 or $KMnO_4$, the reaction proceeds primarily at the *trans*-double bond with formation of the corresponding *trans*-diol and *trans,trans*-tetraol[128]. When cyclododecadienediol (XVI) was oxidised, the unsaturated dialdehyde (XVII) was obtained[129]:

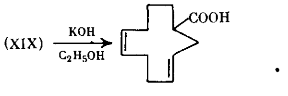


The opening of the epoxy-ring in (XIV) and (XV) takes place readily under the influence of hydrochloric and hydrobromic acids with formation of the corresponding halogenohydrins (XVIII)[114]:

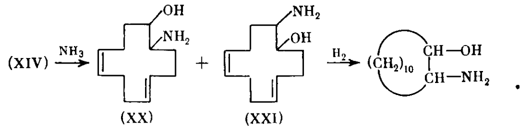


X = Cl or Br.

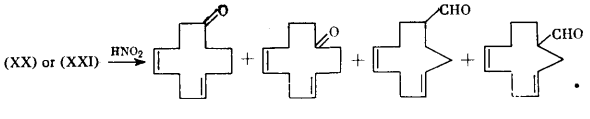
When the halogenohydrins (XVIII) are oxidised by the chromic acid mixture, it is possible to obtain high yields of the unsaturated halogeno-ketones (XIX). The halogenohydrins and the halogeno-ketones obtained from the epoxide (XIV) consist of a mixture of isomers with different positions of the OH group, the halogen atom, and the carboxy-group relative to the *cis*- and *trans*-double bonds in the ring[114]. Cycloundecadienecarboxylic acid has been obtained from the ketones (XIX) by the Favorskii reaction[114]:



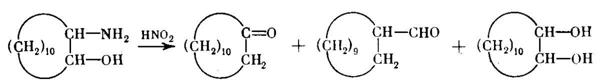
On heating with an aqueous ammonia solution, the epoxide (XIV) gives rise to a mixture of two isomeric *cis*-amino-alcohols (XX) and (XXI)[130], which form *cis*-1,2-aminocyclododecanol on hydrogenation:



When (XX) and (XXI) were deaminated, a mixture of isomeric cyclododecadienones and formylcycloundecadienes was isolated[130]:

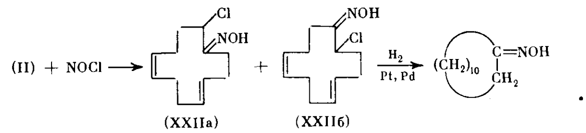


Regardless of the configuration of the initial compound, the deamination of *cis*- and *trans*-2-aminocyclododecanols leads to a mixture of cyclododecanone, formylcycloundecane and *cis*-1,2-cyclododecanediol in equal proportions[130]:

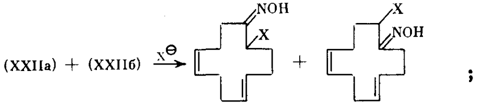


When α-aminocyclododecanecarboxylic acid is deaminated, α-hydroxycyclododecanecarboxylic acid is obtained in a quantitative yield[131].

Nitrosyl chloride readily adds to (II) at a *trans*-double bond with formation of two products (XXII, a and b)[132–140]:

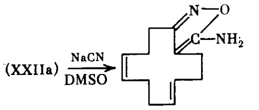


The hydrogenation of chloro-oximes at atmospheric pressure in the presence of platinum and palladium catalysts yields cyclododecanone oxime as the main product[132,133,135]. Several patents[141–144] and another communication[140] describe chlorine exchange reactions involving α-chlorocyclododecadienone oxime. When (XXIIa) and (XXIIb) are treated with nucleophiles, products resulting from the substitution of a chlorine atom are obtained in a high yield[142]:

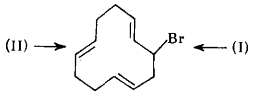


X = C_2H_5O, CH_3O, C_2H_5S, CH_3COO, or R_2N.

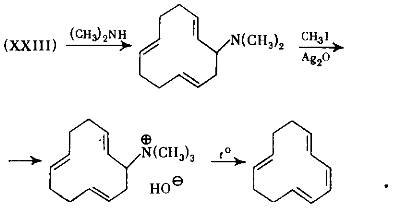
The reaction of (XXIIa) with sodium cyanide in dimethyl sulphoxide (DMSO) leads to the formation of the corresponding aminoisoxazoles[140], for example:



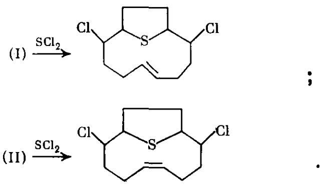
Allylic bromination of (II) by *N*-bromosuccinimide proceeds with isomerisation involving the *cis*-double bond and leads to bromocyclododecatriene (XXIII), which is also obtained on allylic bromination of (I)[58]:



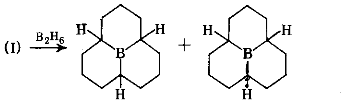
Treatment of the bromo-derivative (XXIII) with ammonia, dimethylamine, and potassium acetate gives rise to substitution products[58], for example:



Acylation of (II) via the Kondakov reaction yields a mixture of 1-acyl-2,5-9- and 1-acyl-1,5,9-cyclododecatrienes[145]. Reactions involving the addition of sulphur dichloride to (I) and (II) and leading to dichlorothiabicyclotridecenes are of interest[146,152]:

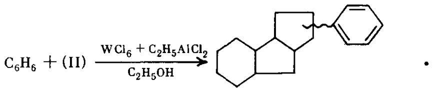


The chlorine atoms in these compounds are readily replaced by cyano- and acetoxy-groups[152]. The hydroboration of (II) gives rise to a mixture of the *cis*- and *trans*-isomers of 9*b*-boraperhydrophenalene (XXIV, a and b) together with 9*b*-boraperhydrobenzo[*ed*]azulene. The latter is converted into *cis*-9*b*-boraperhydrophenalene on heating[147,148]:



(XXIVa) (XXIVb) .

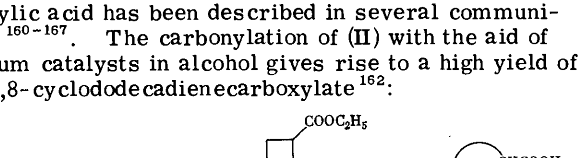
(XXIVa) readily reacts with LiH to form an addition product, which is an effective stereoselective reducing agent for cyclic ketones[149,150]. Trichlorosilane and dichloromethylsilane add to (II) preferentially at the *trans*-double bond in the presence of platinum[151]. When (II) is treated with hydrogen bromide in the presence of benzoyl peroxide, 9-halogeno-1,5-cyclododecadiene is obtained[154]. The reaction of (II) with nitrogen oxides has been described[155]. When (II) reacts with benzene in the presence of the $WCl_6 + C_2H_5AlCl_2 + C_2H_5OH$ system, phenyltricyclo$[6,4,0,0^{2,6}]$dodecane is formed[156]:



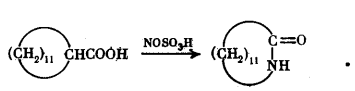
Incomplete ozonisation of (I) and (II) with subsequent cleavage of the ozonide leads to deca-3,7-diene-1,10-dicarboxylic acid and the corresponding dialdehyde[157,158]:

$$\text{(I) or (II)} \xrightarrow{O_3} HOOC(CH_2)_2CH{=}CH(CH_2)_2CH{=}CH(CH_2)_2COOH \ .$$

It has been established that ozone attacks (I) and (II) at the same rate[159]. The carbonylation of (I) and (II) under the influence of CO in the presence of metal (Ni, Co) carbonyls and palladium complexes with formation of cyclododecanecarboxylic acid has been described in several communications[160-167]. The carbonylation of (II) with the aid of palladium catalysts in alcohol gives rise to a high yield of ethyl 4,8-cyclododecadienecarboxylate[162]:

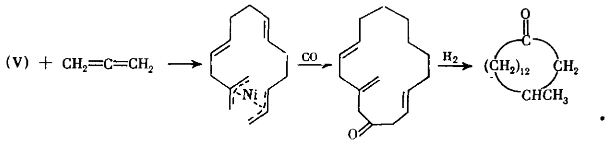


When cyclododecanecarboxylic acid is acted upon by nitrosylsulphuric acid, ω-dodecalactam is obtained in a high yield[168,169]:

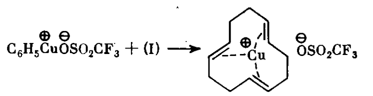


Certain other reactions of cyclododecanecarboxylic acid have been described[170,171]. (I) and (II) react on heating with maleic anhydride to form 1 : 1 adducts[172-174]. The condensation of (II) with cyclopentadiene has been described[175].

Metal complexes of (I) and (II) are known. A π-allyl complex of (V), which reacts with allene, has been described[176,177]. Subsequent reactions of the product lead to the synthesis of DL-muscone:



π-Complexes of palladium $(C_{12}H_{17-19}PdCl)_2$[178] and copper[179,180] have been obtained and a copper complex, synthesised by the reaction[181,182]



has been synthesised.

When a heptane solution of (I) is refluxed with bis(trimethylgermyl)tetracarbonylruthenium, a mixture of products with different structures is formed[183]. The reaction of (I) with dodecacarbonyltriruthenium also leads to a mixture of products having different compositions[184]:

$$\text{(I)} + Ru_3(CO)_{12} \rightarrow HRu_3(CO)_9(C_{12}H_{15}) + HRu_3(CO)_9(C_{12}H_{17}) + \\ + HRu(CO)_7(C_{24}H_{34}) + Ru_4(CO)_{10}(C_{12}H_{16}) \ .$$

Analogous complexes have been obtained for rhodium[185,186], iridium[187], nickel[40,48], and iron[188].

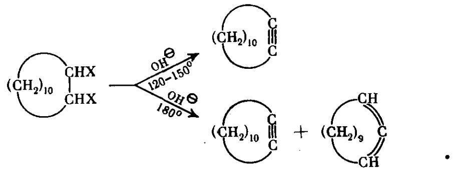
Silver nitrate forms with (I) three types of adducts in which one, two, or three *trans*-double bonds are coordinated to the silver ion[56,68,189]:

$$C_{12}H_{18}\cdot AgNO_3, \ C_{12}H_{18}\cdot 2AgNO_3, \ C_{12}H_{18}\cdot 3AgNO_3.$$

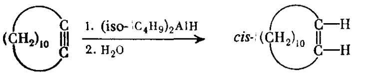
When (II) reacts with a silver ion, only the two *trans*-double bonds are coordinated, while the *cis*-double bond is unaffected[68,189].

IV. SYNTHESES BASED ON *cis*- AND *trans*-CYCLODODECENES

Several methods for the synthesis of *cis*- and *trans*-cyclododecenes (XXV) and (XXVI) are known. It was noted above that they are obtained on selective hydrogenation of (I) and (II)[83,84,91-94] in the presence of homogeneous catalysts or when (II) is acted upon by di-imide[80]. A mixture of (XXV) and (XXVI) is formed when HCl is eliminated from chlorocyclododecane in the presence of iron-containing catalysts[190]. Dehalogenation of 1,2-dichloro- or 1,2-dibromo-cyclododecane by sodionaphthalene or sodiobiphenyl gives a 90% yield of a mixture of (XXV) and (XXVI)[191]. When 1,2-dihalogenocyclododecanes are heated in the presence of alkalis at 150°C, only cyclododecyne is formed[192-194]. On raising the temperature to 180°C, a mixture of 28% of 1,2-cyclododecadiene and 72% of cyclododecyne was isolated[193]:

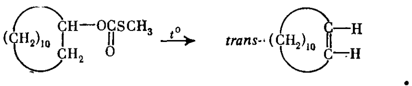


An analogous mixture was obtained after double dehydrobromination of dibromocyclododecane with alcoholic alkali[130]. When cyclododecyne is reduced by (iso-C_4H_9)$_2$.AlH, mainly 6-cyclododecene is formed[193]:



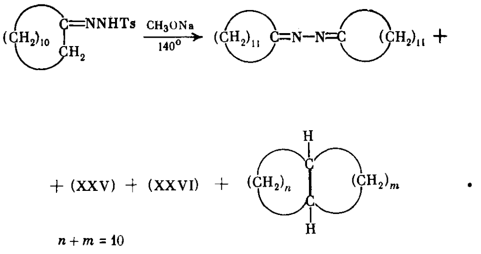
(XXV)

A mixture of 90% of *cis*- and 10% of *trans*-cyclododecyne is formed on decomposition of cyclododecenone semicarbazone by alkoxides at 180–240°C.[195,196] Pyrolysis of cyclododecyl acetate at 550°C leads to a mixture of isomers (XXV) and (XXVI) in proportions of 1 : 5.[197] When (XXV) or (XXVI) is heated in acetic acid at 80–130°C, *cis–trans* isomerisation takes place with formation of an equilibrium mixture containing approximately equal amounts of (XXV) and (XXVI)[197]. Contrary to the Chugaev rule, the decomposition of *O*-cyclododecyl *S*-methyl thiocarbonate gives rise to *trans*-cyclododecene[130]:

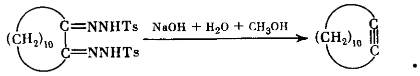


(XXVI)

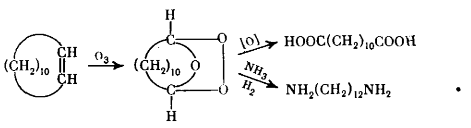
When cyclododecanol was heated to 250–270°C in the presence of toluene-*p*-sulphonic acid, a high yield of cyclododecene was obtained[198]. The reaction of cyclododecene with *N*-bromosuccinimide and subsequent dehydrobromination of the product in pyridine or quinoline result in the formation of 1,3-cyclododecadiene[199]. The dehydration of 6-hydroxy- or 6-acetoxy-cyclododecanone in the presence of $Zn_3(PO_4)_2$ and Fe_2O_3, leading to cyclododec-5-en-1-one, has been described. In the presence of alkyllithium in tetrahydrofuran (THF), cyclododecanone *N,N*-ditosylhydrazone decomposes to form a mixture of *cis*- and *trans*-cyclododecene and cyclododecanone[201]. When cyclododecanone tosylhydrazone is heated in the presence of sodium methoxide, the decomposition leads mainly (to the extent of 60%) to cyclododecanone azine[202]:



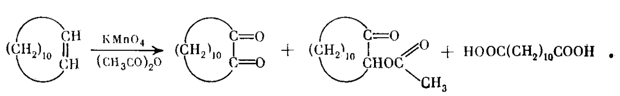
On photolysis of 1,2-cyclododecanedione bistosylhydrazone in an alkaline solution, cyclododecyne was isolated in 53% yield[203]:



Ozonisation with subsequent conversion into decane-1,10-dicarboxylic acid[204–206] and 1,12-diaminododecane[207] is an important reaction of cyclododecene:

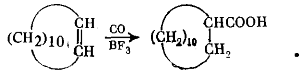


When cyclododecene is oxidised by nitric acid in the presence of ammonium vanadate, considerable amounts of nonane-1,9-dicarboxylic acid are formed together with decane-1,10-dicarboxylic acid[208]. Catalytic oxidation of cyclododecene by hydrogen peroxide in the presence of Re_2O_7 takes place with dissociation of the C=C bond and yields decane-1,10-dicarboxylic acid[209]. Oxidation with potassium permanganate in acetic anhydride leads to 1,2-cyclododecanedione (48%) and other products[210]:

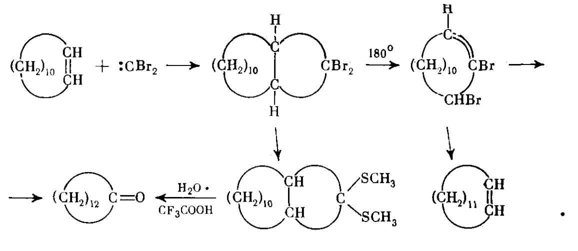


In an alkaline medium in the presence of catalytic amounts of benzyltriethylammonium chloride, *trans*-1,2-cyclododecanediol is formed in 50% yield[211].

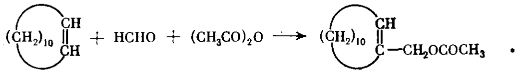
Cyclododecanecarboxylic acid has been obtained from cyclododecene by the Koch reaction[167]:



Dibromocarbene adds smoothly to cyclododecenes with formation of 13,13-dibromobicyclo[10,1,0]tridecane, from which cyclotridecanone[212,213] and cyclotridecene[212] were obtained:

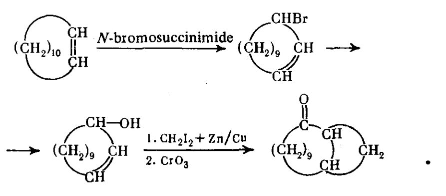


Metathesis of cyclododecene in the presence of the WCl_6 + $C_5H_5AlCl_2$ system yielded unsaturated cyclic hydrocarbons containing 24, 36, and 48 carbon atoms in the ring[214]. The condensation of cyclododecene and (II) with formaldehyde has been described[215]:

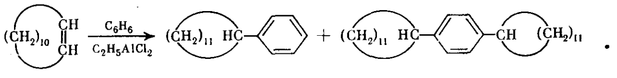


When cyclododecene reacts with paraformaldehyde, *trans*-bicyclo[10,3,0]-2-oxa-14-pentadecene is formed[216].

trans-Bicyclo[10,1,0]-2-tridecanone has been obtained from cyclododecene[217]:

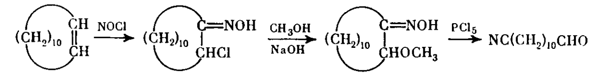


When cyclododecene is acted upon by NO in the presence of O_2, 1-nitroso-2-nitrocyclododecane is obtained. It rearranges on heating in DMF to give 2-nitrocyclododecanone oxime. 1,12-Diaminododecane and ω-nitrolauric acid were obtained from the latter[218]. Cyclododecene undergoes a Friedel–Crafts reaction with benzene and its homologues to form alkylation products[219,220]:



Pyrolysis of (XXV) and (XXVI) results in the cleavage of the ring with formation of 1,8-nonadiene and 1,11-dodecadiene and also in isomerisation involving the double bonds[221]. When cyclododecene was treated with atmospheric oxygen in t-C_4H_9OH in the presence of manganese naphthanate, 1,2,3-cyclododecanetriol was obtained[222]. Photochemical cycloaddition of the olefins (XXV) and (XXVI) to dichlorovinylene carbonate leads to three stereoisomeric carbonates of dichlorobicyclo[10,2,0]-2,3-tetradecanediols[223].

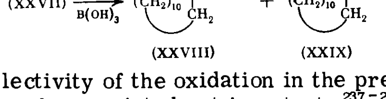
The synthesis of ω-cyanoundecanoic aldehyde from (XXV) and (XXVI) via the mechanism



is of great interest[224]. The reaction of cyclododecene with B_2H_6 yielded the corresponding tri(cyclodecyl)borane[225]. When cyclododecene was treated with nitrogen oxides and air, α-nitrocyclododecanone was obtained in a high yield[226-230]. The mechanism of the oxidation of (XXV) and (XXVI) by molybdenum peroxide has been investigated[231]. A study has been made of the kinetics of the hydrogenation of (XXV) and (XXVI) to cyclododecane in the presence of platinum and palladium blacks[232]. (XXV) and (XXVI) form π-allyl complexes with palladium chloride[233]. The structure of the complex of *trans*-cyclododecene with $AgNO_3$, having the composition (*trans*-$C_{12}H_{22})_2.AgNO_3$, has been investigated[234]. On heating with perfluorobutyne, *cis*, *trans*-1,3-cyclododecadiene gives rise to a mixture of two bicyclic products[235].

V. SYNTHESES OF CYCLODODECANE DERIVATIVES

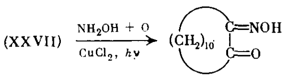
The methods of synthesis of cyclododecane derivatives are of great significance, since the preparation of the industrially important decane-1,1-dicarboxylic acid, 1,12-diaminododecane, and ω-dodecalactam is based on them. The oxidation of cyclododecane (XXVII) by atmospheric oxygen to cyclododecanol (XXVIII) and cyclododecanone (XXIX) has been studied in detail. When (XXVII) is oxidised by oxygen in the presence of boric acid or boron trioxide, a mixture of 80% of (XXVIII), 8–10% of (XXIX), and 10% of polyfunctional oxygen-containing compounds (conversion 30–35%) is formed[69,236]:



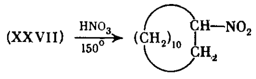
(XXVIII) (XXIX)

The high selectivity of the oxidation in the presence of boric acid has been pointed out in patents[237-239]. A greater amount of the ketone (XXIX) is formed in the presence of manganese or cobalt salts[240,241]. When (XXVII) was oxidised by oxygen in the absence of boric acid, it was found that at the beginning of the process cyclododecyl hydroperoxide, (XXIX), and (XXVIII) accumulate simultaneously[242-245]. After the attainment of the maximum, the concentration of the hydroperoxide falls owing to its thermal decomposition. This results in the formation of a mixture of 70% of (XXIX) and 30% of (XXVIII). Cyclododecane is oxidised to cyclododecyl hydroperoxide in the presence of alkali metal salts[246-248]. A study of the mechanism of the decomposition of cyclododecyl hydroperoxide showed[249] that considerable amounts of undecane and undecyl alcohol are formed in an inert medium, while in the presence of O_2 hardly any undecane is formed. The oxidation of (XXVII) by nitrogen dioxide to decane-1,10-dicarboxylic acid has been reported[250,251].

Treatment of (XXVII) by hydroxylamine and oxygen under irradiation leads to 1,2-cyclododecanedione monoxime[252]:

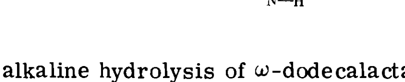


Nitrocyclododecane was obtained in the liquid-phase nitration of (XXVII) by nitric acid[168,253,254]:

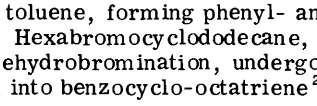


Nitrocyclododecane was also obtained on hydrogenation of 3-nitrocyclododecene[255]. When nitrocyclododecane is treated with a solution of potassium hydroxide, the potassium salt of *aci*-nitrocyclododecane is formed and is converted into *aci*-nitrocyclododecane on acidification[254,256]. This *aci*-form is stable and does not change even on recrystallisation[254]. When nitrocyclododecane was hydrogenated, aminocyclododecane and cyclododecanone oxime were obtained[254,257]. When the potassium salt of *aci*-nitrocyclododecane was treated with $H_2NOH.HCl$, cyclododecanone oxime is formed in a high yield[254].

The hydrolysis of a nitrocyclododecane salt results in the formation of cyclododecanone[254,258,259]. The conversion of nitrocyclododecane into ω-dodecalactam at a high temperature in the presence of certain metal oxides has been described[260]. Numerous studies have been devoted to the photonitrosation of (XXVII) to cyclododecanone oxime[139,153,168,261-266] and to the isomerisation of cyclododecanone oxime to ω-dodecalactam, which is the initial compound in the synthesis of polyamide-12[261,262,267-271]:

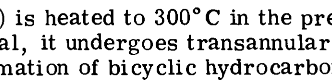


Nitrododecalactam has been obtained by treating α-nitrocyclododecanone oxime with concentrated sulphuric acid at 40-50° C:[272]



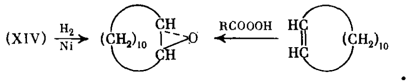
The acid or alkaline hydrolysis of ω-dodecalactam results in the formation of ω-aminododecanoic acid[11,273,274].

The photochemical chlorination of (XXVII) to monochlorocyclododecane has been investigated[75,275,276]. Monochlorocyclododecane undergoes the Friedel–Crafts reaction in benzene and toluene, forming phenyl- and tolyl-cyclododecanes[277]. Hexabromocyclododecane, obtained from (I) and (II) on dehydrobromination, undergoes an unusual transformation into benzocyclo-octatriene[278]:



When (XXVII) is heated to 300° C in the presence of platinised charcoal, it undergoes transannular dehydrocyclisation with formation of bicyclic hydrocarbons[279].

Epoxycyclododecane (XXX) has been obtained by the hydrogenation of the double bonds in epoxycyclododecadiene[68] and by the epoxidisation of cyclododecene by peracids[75,130]:



(XXX)

The *cis-* and *trans*-oxides are formed from *cis-* and *trans*-cyclododecene. Catalytic hydrogenation of (XXX) over Raney nickel[11,68,75] leads to the formation of cyclododecanol and cyclododecanone:

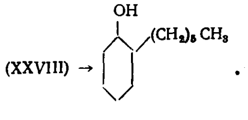
$$(XXX)\ \xrightarrow[Ni]{H_2}\ (XXVIII) + (XXIX)\,.$$

Isomerisation of the epoxide (XXX) under the influence of LiBr[125] or MgI_2[124] leads to cyclododecanone:

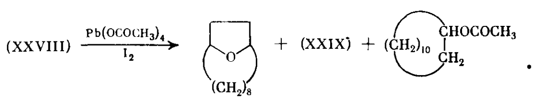
$$(XXX)\ \xrightarrow{MgI_2}\ (XXIX)\,.$$

Cyclododecanol has been obtained by hydrating cyclododecene with sulphuric acid[280] and also on hydrogenation and hydrolysis of 1-acetoxy-5,9-*trans*,*trans*-cyclododecadiene[273]. Dehydrogenation of cyclododecanol at 240–250°C under the influence of catalysts (Raney nickel, Cu/Cr, Ni/Al_2O_3, Cu/SiO_2) leads to the formation of cyclododecanone in a high yield[11,70,240,281]. The synthesis of cyclododecanone by the hydrolysis of cyclododecanone oxime has been described[258,259].

Decane-1,10-dicarboxylic acid is formed in a high yield when cyclododecanol or its mixture with cyclododecanone is acted upon by nitric acid in the presence of ammonium metavanadate[11,110,282] or V_2O_5.[283] It has been stated in patents[284,285] that the oxidation of cyclododecanol is accompanied by nitration, which resulted in the isolation of ω,ω-dinitrododecanoic acid; however, the addition of copper powder to the oxidation reaction prevents the formation of nitro-acids[285]. When cyclododecanol is treated with a mixture of $FSO_3H-SbF_5-SO_2$, it isomerises to hexylcyclohexanol[286]:



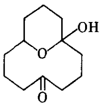
The oxidation of cyclododecanol by lead tetra-acetate in the presence of iodine gives rise to a mixture of oxygen-containing products in which 13-oxabicyclo[8,2,1]dodecane (XXXI) predominates[287]:



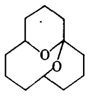
(XXXI)

Oxidation in the absence of iodine leads mainly to acetoxycyclododecane.

When cyclododecanediol is heated in the presence of Raney nickel, 2-hydroxycyclododecanone is formed[288], while catalytic oxidation in the presence of $[(C_6H_5)_3P]_3RuCl_2$ and benzaldehyde yields 1,2-cyclododecanedione[289]. Methods for the preparation of 2-alkoxy-1-alkylcyclododecanes[290] and cyclododecylamides[291], which exhibit pharmacological activity, have been described. 1-(Dialkylaminoalkyl)cyclododecyl carboxylates[292] and the esters of 1-(aminoalkyl)cyclododecanol possess bactericidal properties[293]. The oxidation of *cis*,*cis*,*trans*-1,5,9-cyclododecanetriol by the Brown method proceeds with a transannular interaction and leads to the hemiacetal (XXXII) and the acetal (XXXIII) in proportions of 43 : 57.[294]



(XXXII)



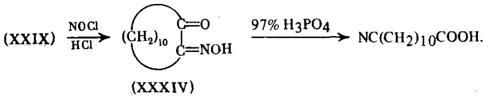
(XXXIII)

VI. SYNTHESES BASED ON CYCLODODECANONE

Numerous compounds have been synthesised on the basis of cyclododecanone (XXIX) and many interesting reactions have been carried out. As stated above, (XXIX) is obtained by the dehydrogenation of cyclododecanol (XXVIII)[11,70,240,281], the isomerisation of epoxycyclododecane (XXX)[124,125], the hydrolysis of cyclododecanone oxime[258,259], and the oxidation of cyclododecane[69,236–248] and cyclododecanol[69]. Several studies have been devoted to the synthesis of cyclododecanone oxime from (XXIX) and its conversion into ω-dodecalactam[11,70,295–297].

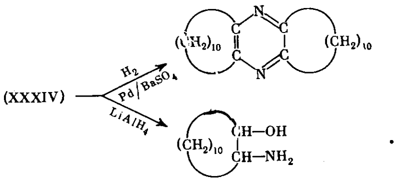
The reaction of hydroxylamine with cyclododecanone under the influence of hydroxylammonium chloride or sulphate takes place readily and in a quantitative yield in the presence of bases (ammonia, potassium or sodium carbonate)[11,70,295,296]. When industrial hydroxylammonium sulphate, containing ammonium sulphate and sodium sulphate, is used, the conversion of cyclododecanone into the oxime takes place without the addition of bases, because sulphuric acid is bound into acid ammonium and sodium salts[11,295]. The reaction with hydroxylamine is carried out in alcoholic, aqueous alcoholic, and aqueous media, a higher temperature being necessary in an aqueous medium. Cyclododecanone oxime forms a 2 : 1 complex with $SnCl_4$.[298]

The mechanism of the Beckmann rearrangement in cyclododecanone oxime has been investigated and it has been found that the process proceeds via a unimolecular mechanism[299]. α-Chlorocyclododecanone oxime is readily obtained when nitrosyl chloride adds to cyclododecene[300]. The substitution of the chlorine atom in α-chlorocyclododecanone oxime by alkoxy- and amino-groups has been described[301–304]. On treatment of (XXIX) with NOCl or $RONO_2$ in the presence of HCl or sodium alkoxide, cyclododecanedione monoxime (XXXIV) is formed in a high yield[305]; it rearranges smoothly to 11-cyanoundecanoic acid under the influence of phosphoric acid[306,307]:



(XXXIV)

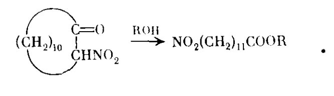
The hydrogenation of (XXXIV) yielded bis-2,3,5,6-decamethylenepyrazine[130]:



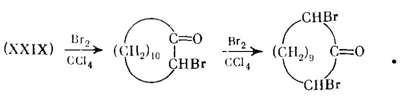
The reaction of (XXIX) with NOCl and ethanol in SO_2 leads to the cleavage of the ring via the mechanism[308]:

$$(XXIX) + NOCl + C_2H_5OH \xrightarrow{SO_2} HON{=}CH(CH_2)_{10}COOC_2H_5 .$$

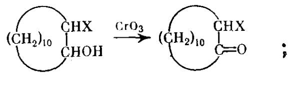
α-Nitrocyclododecanone is obtained by the hydrolysis of its oxime with hydrochloric acid[309]. The alcoholysis of α-nitrocyclododecanone results in the formation of ω-nitrododecanoate esters[310]:



When (XXIX) is brominated, monobromo- or dibromocyclododecanone[311] is obtained:

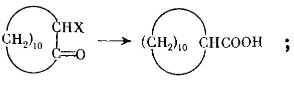


Monohalogenocyclododecanones are readily formed on oxidation of the corresponding halogenohydrins[114]:



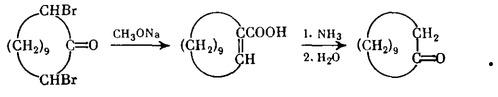
X = Cl, or Br.

The Favorskii rearrangement of α-halogenocyclododecanones under the influence of alcoholic alkali leads to the formation of cycloundecanecarboxylic acid[114]:

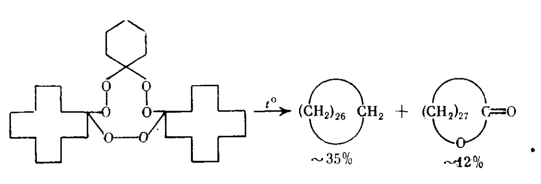


X = Cl, or Br.

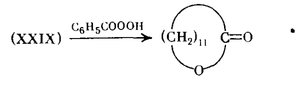
Under these conditions, α,α′-dibromocyclododecanone gives rise to cycloundecenecarboxylic acid, which has been converted into cycloundecanone[311,312]:



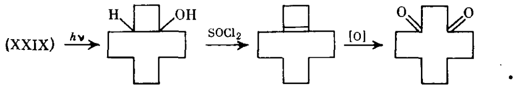
The oxidation of (XXIX) by hydrogen peroxide in the presence of SeO_2 leads to cycloundecanecarboxylic acid[313]. Cyclododecanone peroxide has been obtained by treating (XXIX) dissolved in carboxylic acids with H_2O_2.[314,315] In the presence of cyclic ketones bis(cyclododecylidene) cycloalkylidene triperoxides are formed[316] and their thermal decomposition in chlorobenzene leads to macrocyclic compounds, for example:



Perbenzoic acid[317-319], Caro's acid, and hydrogen peroxide in sulphuric acid[318] were used to oxidise (XXIX) to dodecanolide:



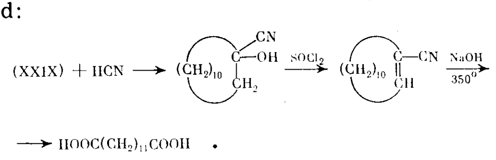
Irradiation of (XXIX) results in a transannular rearrangement with formation of bicyclo[8,2,0]dodecan-1-ol[320,321]:



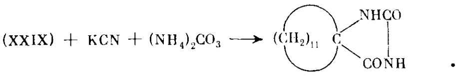
On heating cyclododecanone and cyclododecanol with alkalis to 350°C, a mixture of lauric and nonane-1,9-dicarboxylic acid is formed in 90% yield[322-324]:

$$(XXVIII) + (XXIX) \xrightarrow[350°]{KOH} CH_3(CH_2)_{10}COOH + HOOC(CH_2)_9COOH .$$

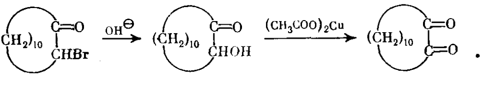
The addition of hydrocyanic acid to (XXIX) takes place readily in the presence of $(C_2H_5)_3N$ with formation of a cyanohydrin[325-327], from which cyclododecanecarboxylic acid[326], cyclotridecanone[327], and brassylic acid[325] were obtained:



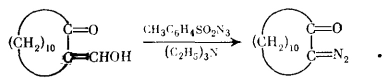
The formation of hydantoins from cyclododecanone or cyclododecenones has been described[328]:



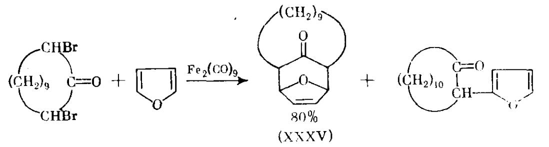
1,2-Cyclododecanedione is formed in a high yield on heating hydroxycyclododecanone with copper diacetate[329,330]:



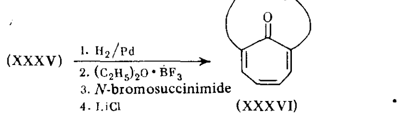
Diazocyclododecanone has been obtained by the reaction[331]:



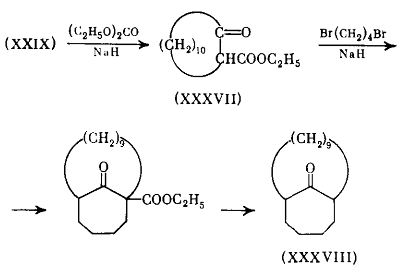
α-Halogenocyclododecanones are readily reduced to cyclododecanone in the presence of LiI and $(C_2H_5)_2O.BF_3$.[332] The reaction of α,α′-dibromocyclododecanone with furan in the presence of $Fe_2(CO)_9$ takes place in an interesting manner[333]:



(XXXV) has been converted via a series of stages into tropone (XXXVI)[334]:



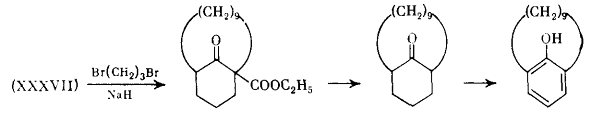
Tropone has been obtained from cyclododecanone also in accordance with another scheme via the ethoxycarbonyl derivative (XXXVII)[335]:



(XXXVII)

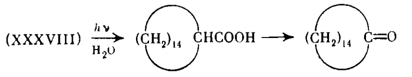
(XXXVIII)

When the ketone (XXXVIII) was brominated and debrominated, tropone was obtained[336]. Metacyclophane (XXXIX) was synthesised similarly[336]:



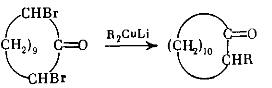
(XXXIX)

Ultraviolet irradiation of the ketone (XXXVIII) led to the formation of cyclopentadecanecarboxylic acid (XL), which was converted into cyclopentadecanone[335,337]:

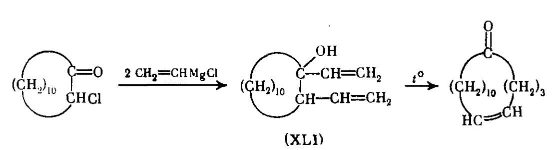


(XL)

A new method has been proposed for the alkylation of α,α'-dibromocyclododecanone with formation of α-alkylcyclododecanones[338,339]:

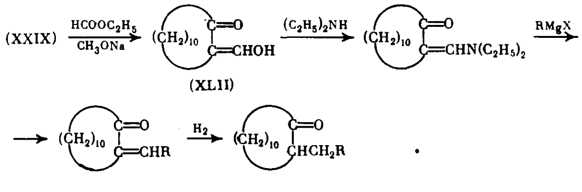


The action of a Grignard reagent on (XXIX) with formation of alkylcyclododecanols has been investigated[202]. Methylcyclododecanone has been obtained by the reaction of bromocyclododecanone with CH_3ZnI in DMSO[202]. The reaction of chlorocyclododecanone with two moles of vinylmagnesium chloride leads to the formation of (XLI), which is converted into 5-cyclohexadecenone after the Cope rearrangement[340,341]:



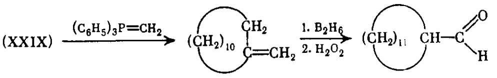
(XLI)

α-Alkylcyclododecanones have been obtained by the formylation of (XXIX) via the mechanism[342]:

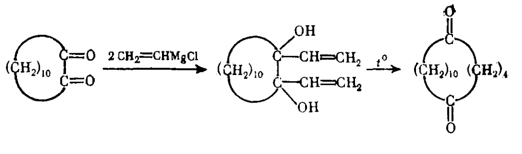


(XLII)

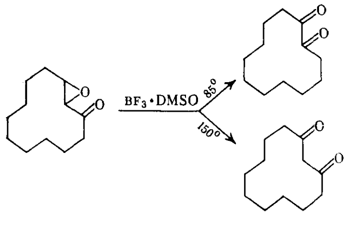
(XLII) undergoes oxidative cleavage by hydrogen peroxide, which leads to brassylic acid[325]. Formylcyclododecane was synthesised from (XXIX) as follows[202]:



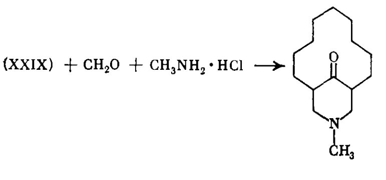
A method has been described for the synthesis of 1,6-cyclohexadecanedione by treating 1,2-cyclododecanedione with vinylmagnesium chloride and a subsequent rearrangement[343]:



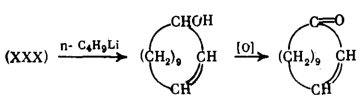
Depending on temperature, the isomerisation of 2,3-epoxycyclododecanone takes place with formation of 1,2- or 1,3-cyclododecanediones[345]:



Methods have been developed for the synthesis of [7]-metacyclophane and its bromo-derivative via the aldol condensation of 1,4-cyclododecanedione[346,347] and [7](2,6)pyridinophane derived from 1,5-cyclododecanedione[348,349]. Cyclododecanone has been made to undergo the Mannich reaction[350,351]:

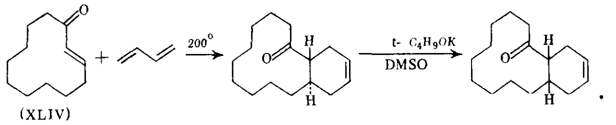


The *cis*- and *trans*-2-cyclododecenones (XLIII) and (XLIV) were obtained from epoxycyclododecane[352]:

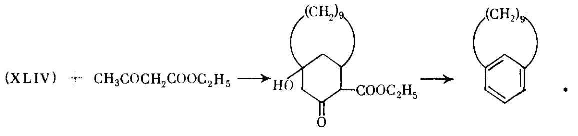


(XLIII) (*cis*-)
(XLIV) (*trans*-).

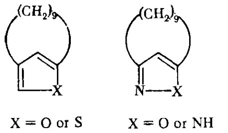
The synthesis of a mixture of *cis*- and *trans*-cyclododecenones by the bromination of cyclododecanone ethylene acetal and subsequent dehydrobromination by t-C_4H_9OK in DMSO has been proposed[353]. *cis*-Cyclododecenone (XLIII) is thermodynamically less stable than the *trans*-isomer (XLIV) and isomerises to the latter[352]. Ultraviolet irradiation of a hexane solution of (XLIV) leads to a mixture of (XLIII) and *cis*-3-cyclododecenone[352]. Diene condensation of (XLIV) with butadiene leads to *trans*-bicyclo[10,4,0]-hexadec-14(15)-en-2-one, which wholly isomerises to the *cis*-isomer on treatment with t-C_4H_9OK:[354]



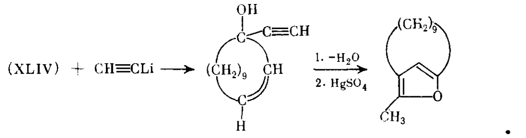
The *cis*-isomer (XLIII) does not undergo diene condensation with butadiene. [9]Metacyclophane and [9](2,4)pyridinophane have been obtained by the reaction of (XLIV) with acetoacetic or cyanoacetic ester and subsequent reactions of the adducts[355]:



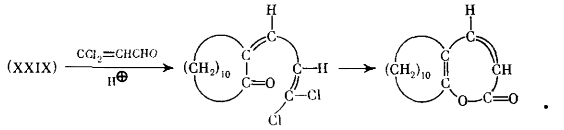
A series of [9]heterophanes have been obtained from (XLIV)[356,357]:



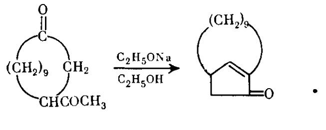
When (XLIV) reacts with hydrazine hydrate and this is followed by dehydrogenation with sulphur, [9](3,5)pyrazolophane is formed, while treatment with lithium acetylide and further cyclisation lead to 11-methyl[9](2,4)furanophane[353]:



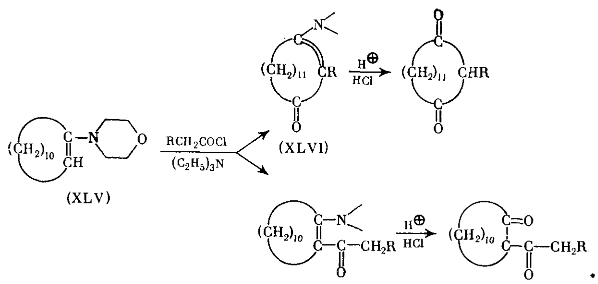
Decamethylene-α-pyrone has been obtained by the condensation of (XXIX) with dichloroacrolein and subsequent cyclisation[358]:



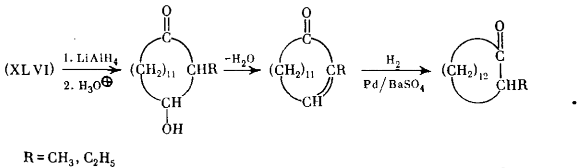
The product of the condensation of 1-methoxycyclododecene with 2-methylbut-3-yne-2-ol undergoes the Cope rearrangement to give 3,3-dimethylallenylcyclododecenone, which isomerises on ultraviolet irradiation to 4-isopropylidenecyclotetradecenone[359]. When 3-acetylcyclododecanone is acted upon by C_2H_5ONa, a bicyclic ketone is formed[360]:



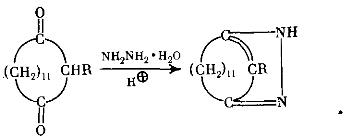
Enamines have found extensive applications in the synthesis of various cyclododecanone derivatives[361-363]. When morpholinocyclododecene (XLV) is treated with carboxylic acid chlorides in the presence of $(C_2H_5)_3N$, 2-alkyl-1,3-cyclotetradecanediones (resulting from the insertion of two carbon atoms in the ring) and acylation products are formed[364,365]:



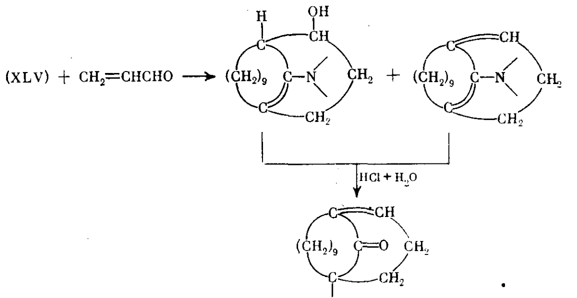
When (XLVI) was treated with lithium tetrahydroaluminate and this was followed by dehydration and hydrogenation, methyl- and ethyl-cyclotetradecanones, which have a strong musk-like scent, were obtained[366]:



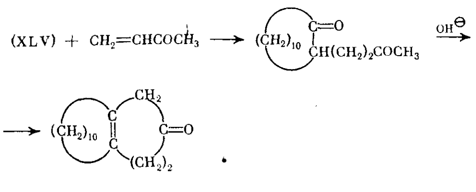
The interaction of 2-alkyl-1,3-cyclotetradecanedione with hydrazine hydrate[364] or 2,4-dinitrophenylhydrazine[366] leads to a pyrazole derivative:



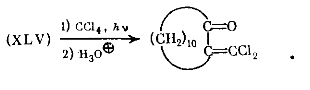
When acrolein acts on (XLV), an interesting reaction takes place[344]:



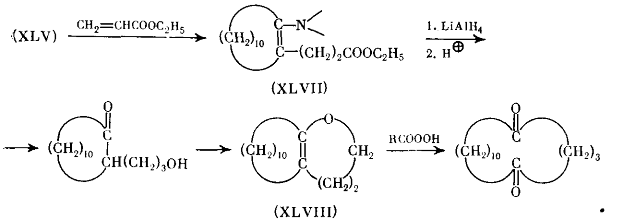
The interaction of (XLV) with methyl vinyl ketone leads to a bicyclic ketone[367]:



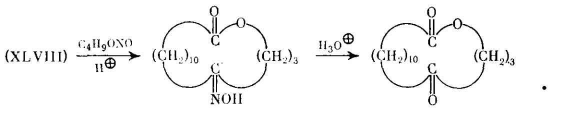
When (XLV) is irradiated with ultraviolet light in the presence of CCl_4, a dichlorovinyl ketone is formed[368]:



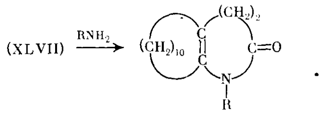
Oxopentadecanolide has been synthesised from (XLV) and ethyl acrylate via the mechanism[369]



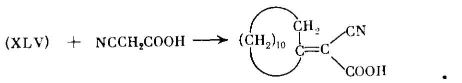
Hydrolysis of (XLVII) leads to β-(2-oxocyclododecyl)propionic acid[344,370]. Ultraviolet irradiation of this acid results in the formation of ω-formyl-4-tetradecenoic acid, whose reduction leads to ω-hydroxypentadecanoic acid[370]. Oxopentadecanolide has also been obtained from (XLVIII) by treatment with butyl nitrite and subsequent hydrolysis[371]:



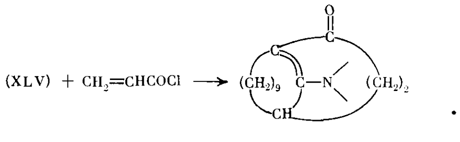
Similarly 1-acetyl-13-hydroxyimino-1-azahexadecan-2-one was obtained from 1-acetyl-2,3-decamethylene-1,4,5,6-tetrahydropyridine[372]. Treatment of the ketoester obtained from (XLVII) with alkylamines leads to the synthesis of bicyclic lactams[373]:



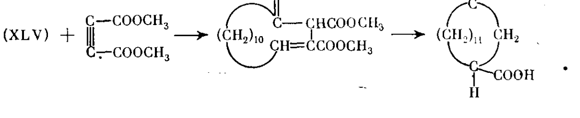
The reactions of (XLV) with a substituted cyclopropene[374] and dibromoacetone have been investigated[375]. The morpholine residue in (XLV) undergoes an exchange reaction with cyanoacetic acid[376]:



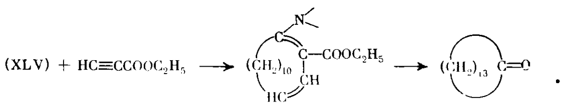
When (XLV) interacts with acryloyl chloride, a bicyclic product is formed[377]:



α-(2-Oxocyclododecyl)acetic acid has been obtained by the reaction of (XLV) with a bromoacetate ester[344]. When pyrrolidinocyclododecene condenses with an ester of acetylenedicarboxylic acid[378], ring expansion takes place with formation of a cyclotetradecenone derivative, which has been converted into 3-carboxycyclotetradecanone[376]:

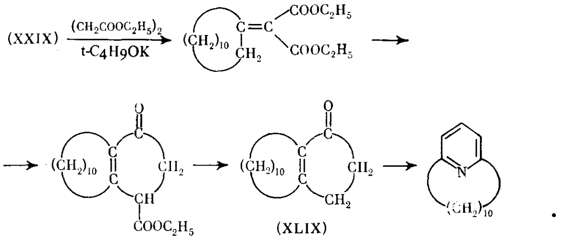


Cyclotetradecanone has been obtained by the reaction of (XLV) with ethyl propiolate[379]:

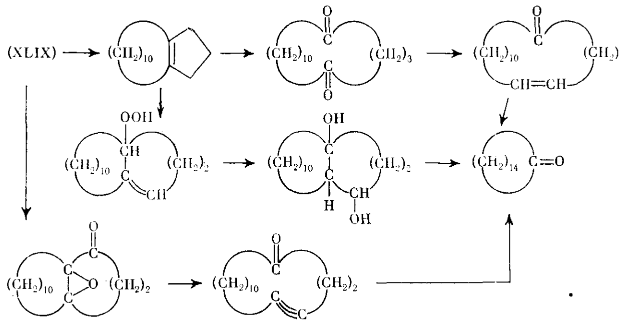


Using this reaction, it is possible to obtain the racemic muscone[380]. A series of methods of synthesis of muscone, cyclopentadecanone (exaltone), pentadecanolide (tibetolide), and methylpentadecanolide (muscolide), which are valuable perfumes, have been developed on the basis of cyclododecanone.

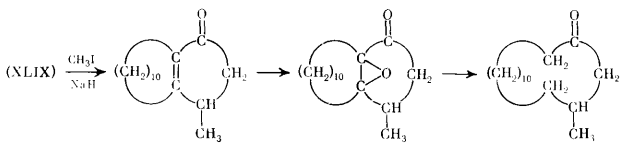
The synthesis of natural muscopyridine from cyclododecanone has been achieved by the Stobbe reaction via (XLIX)[381]:



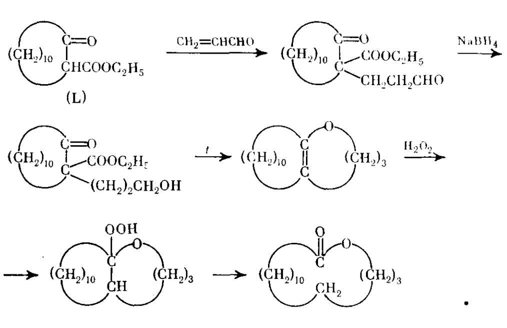
This reaction has served as the basis of a method of synthesis of cyclopentadecanone[382–385]:



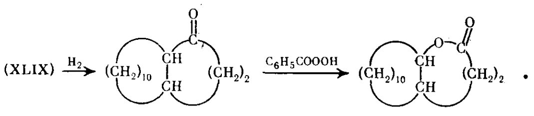
Muscone has been obtained from (XLIX) via the mechanism[383]



A convenient method of synthesis of cyclopentadecanolide via the mechanism[335,337]



has been developed. The methyl analogue of cyclopentadecanolide (muscolide) has been obtained similarly from (L) and methacrolein[328,337]. It has been reported that γ,δ-decamethylene-δ-valerolactone has a strong musk-like scent[386,387]. It has been synthesised via the mechanism



The products of the reaction of cyclododecanone with glycols[388] are components of perfumes.

During the preparation of the review for the press, studies which are of interest were published. An industrial method of synthesising compound (II) (1,5,9-CDT) by a continuous method in the presence of the $(C_2H_5)_2AlCl-TiCl_4$ catalytic system has been developed[389]. A mechanism has been proposed for the cyclisation of butadiene to (I) in the presence of $Ni(C_5H_7O_2)_2 + (C_2H_5)_3Al$.[390] Partial ozonolysis of (I), with subsequent reduction of the peroxycompounds formed by dimethyl sulphide, leads to 1,12-diformyl-*trans*,*trans*-4,8-dodecadiene[391]. Conditions have been found for the selective hydrogenation of (II) to (XXVI) in the presence of $RuCl_2(PPh_3)_3$ activated by $(C_2H_5)_3N$.[392] The reaction of (XXV) and (XXVI) with *N*-bromosuccinimide in the presence of water, methanol, or acetic acid proceeds with formation of 2-bromocyclododecanol, 2-bromo-1-methoxycyclododecane, and 1-acetoxy-2-bromocyclododecane respectively[393]. Oxidation of a mixture of (XXV) and (XXVI) by Jones reagent in the presence of mercury propionate leads to cyclododecanone[394]. It was noticed for the first time that oxidation of cyclododecane by air results in the formation of 2–3% of *trans*-epoxycyclododecane[395]. The isomerisation of epoxycyclododecane to cyclododecanone proceeds with a high yield in the presence of palladium and rhodium catalysts[396]. When epoxycyclododecane is acted upon by formaldehyde in the presence of $AlCl_3$, 13,15-dioxabicyclo[10,3,0]pentadecane and 13,15,17-trioxabicyclo[10,5,0]heptadecane are formed[397]. On ultraviolet irradiation, a mixture of 36% of methyl cycloundecanecarboxylate, 17% of *cis*- and 25% of *trans*-cyclododecenones, and 9% of *cis*-3-cyclododecenone is formed on ultraviolet irradiation of α-diazocyclododecanone[398]; the reaction involving 2-methylcyclododecanone takes place with ring cleavage and the formation of 40% of formyl-12-dodecene[399]. A synthesis of bicyclo-[10,3,0]pentadeca-1(12)-en-13-one and its methyl analogues from cyclododecanone has been proposed[400]. Formylcyclodecane has been obtained from cyclododecanone and ethoxymethylmagnesium chloride[401]. Treatment of 1,5-cyclododecadiene with *N*-bromosuccinimide and subsequent reduction of the product with $LiAlH_4$ lead to 13-oxabicyclo-[8,2,0]dodecane[402].

A method of synthesis of cyclododecanone oxime on heating cyclododecanone with ammonia in the presence of t-butyl hydroperoxide has been described in a patent[403]. A method of synthesis of 1,3- and 1,4-cyclododecanediones from a mixture of *cis*- and *trans*-3-cyclododecenones has been discovered[404]. [10]Paracyclophane has been synthesised from cyclododecene and methyl acetylenecarboxylate[405]. [9](2,4)Pyrrolophane has been synthesised in two ways: (1) by the condensation and cyclisation of 3-formylcyclododecanone with ammonia and (2) by the condensation of chlorocyclododec-2-en-1-one with di(ethoxycarbonyl)-methylamine[406].

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Cyclotrimerisation of Cyano-compounds into 1,3,5-Triazines

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A survey is made of papers on the cyclotrimerisation of substituted monofunctional cyanides X.C:N differing in the structure of the substituent X = H, R, Ar, >N, HO, RO, ArO, HS, RS, Hal. This reaction has been widely used in recent years both in preparative organic chemistry and in large-tonnage industrial manufactures, by virtue of the availability of the initial compounds, the high yields of 1,3,5-triazines, and the simplicity of operation. Attention is paid mainly to recent work to elucidate the influence of substituents X on the reactivity of N⋮C-containing compounds; various mechanisms of cyclotrimerisation are discussed, as well as the effects of catalysts, pressure, and other factors. Consideration is given not only to homocyclotrimerisation but also to mixed cyclotrimerisation of cyanide derivatives and the influence of the reaction conditions on the structure of the resulting 1,3,5-triazines. A list of 247 references is included.

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I. INTRODUCTION

1,3,5-Triazines are important products of modern organic chemistry. They are widely used as intermediates in dye chemistry and in the paper, paint and varnish, and pharmaceutical industries, as herbicides and as monomers for the synthesis of thermostable polymers, and in several other branches of the national economy.

The most promising method for the industrial synthesis of 1,3,5-triazines is the cyclotrimerisation of compounds containing a nitrogen–carbon triple bond, since this reaction usually occurs selectively to give high yields of the final products. In industry cyclotrimerisation has been used to obtain such compounds as cyanuric acid, melamine, cyanuric chloride, etc. The cyclotrimerisation of several compounds containing an N⋮C bond was known as early as the nineteenth century, but the largest amount of research has been conducted during recent years. Attention has been concentrated mainly on studying the mechanisms of cyclotrimerisation, the synthesis of new derivatives of 1,3,5-triazine, the selection of various catalytic systems, etc. Furthermore, a long series of papers has appeared on the synthesis of highly heat-resistant and thermostable polymers from N⋮C-containing monomers.

In several of the earlier reviews and monographs[1–5] containing information on 1,3,5-triazines little attention was paid to cyclotrimerisation. Most of these surveys were published 15–20 years ago, and do not reflect advances made during recent years.

The present Review surveys published results on the cyclotrimerisation of cyanide derivatives in which the cyano-group is attached to various atoms and radicals (H, R, RO, RS, R_2N, Hal). Data on the conditions for the cyclotrimerisation of particular classes of compounds are summarised in tables. Attention is paid mainly to recent studies of mechanisms, the influence of the nature of substituents attached to cyano-groups on their electrophilic character, and the tendency to undergo this reaction. The cyclotrimerisation of compounds containing two or more functional groups to give polymers has been discussed in detail in several recent reviews[6–8], and therefore will not be considered here.

II. 1,3,5-TRIAZINE FROM HYDROGEN CYANIDE

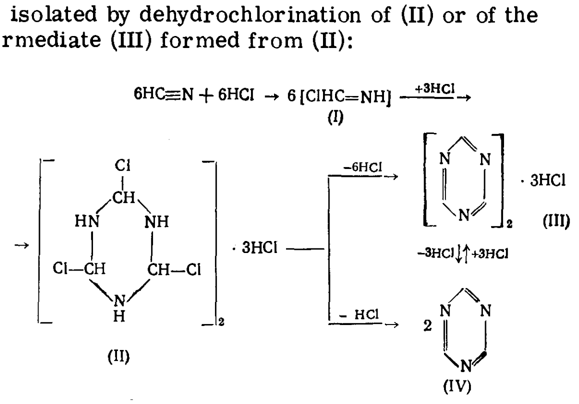
Since 1,3,5-triazine, unlike most of its derivatives, is highly reactive towards nucleophiles, it could not be identified until 1954.[9,10] This compound was obtained by Nef[11] more than a half-century ago, but it was then regarded as a dimer of hydrogen cyanide.

The mechanism of the formation of 1,3,5-triazine by the action of hydrogen chloride on hydrogen cyanide was investigated by Grundmann and Kreutzberger[12]. They suggested that initial addition of equimolecular quantities of the reactants is followed by spontaneous trimerisation of the adduct (I)† to bis-(2,4,6-trichlorohexahydro-1,3,5-triazine) trihydrochloride (II); 1,3,5-triazine (IV)

---

†Kreutzberger has since[4] attributed the structure $[HC⋮NH]^+Cl^-$ to the adduct (I).

was isolated by dehydrochlorination of (II) or of the intermediate (III) formed from (II):

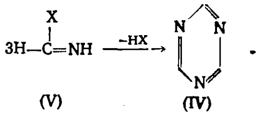


The yield of 1,3,5-triazine from the trimerisation of hydrogen cyanide in the presence of hydrogen chloride is 55-60%.[9,12,13]

Table 1. Synthesis of 1,3,5-triazine by the cyclocondensation of compounds (V).

X	Reaction conditions			Yield, wt.%	Ref.
	catalyst	T, °C	p, atm		
C_2H_5O	NaOH	—	—	10	11
HS	—	80	vacuum	20	15
H_2N	R_3N	150—250	0.02	3—72	12, 16, 17
$C_6H_5CH_2$—O	$C_6H_5N(C_2H_5)_2$	80	0.01	50	18

1,3,5-Triazine can also be obtained[10,14] by the thermal or base-catalysed (Table 1) cyclocondensation of compounds (V):

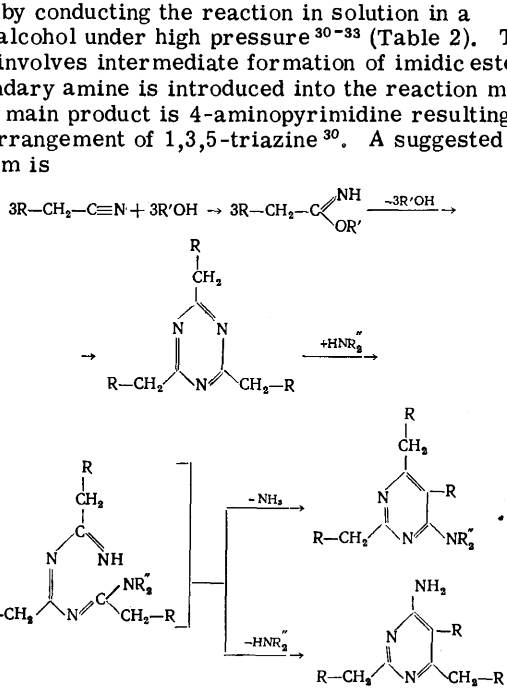


III. 2,4,6-TRIALKYL-1,3,5-TRIAZINES FROM ALKYL CYANIDES

1. 2,4,6-Trialkyl-1,3,5-triazines from Unsubstituted Alkyl Cyanides

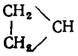
Repeated attempts were made[19-29] to synthesise trialkyltriazines by the cyclotrimerisation of alkyl cyanides R.CN, but few successes were achieved. Thus the action of strong bases on alkyl cyanides involves deprotonation of the α-carbon-hydrogen bond followed by addition of the next cyanide molecules to form aminopyrimidine rings[19-29].

1,3,5-Triazines have been obtained from aliphatic cyanides by conducting the reaction in solution in a primary alcohol under high pressure[30-33] (Table 2). The reaction involves intermediate formation of imidic esters. If a secondary amine is introduced into the reaction mixture, the main product is 4-aminopyrimidine resulting from rearrangement of 1,3,5-triazine[30]. A suggested[32] mechanism is



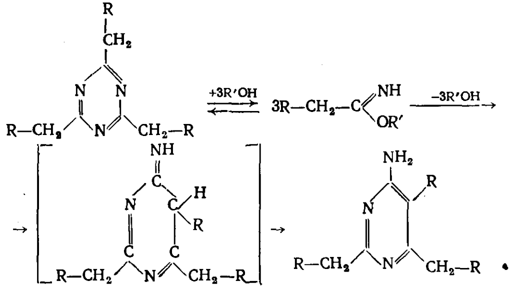
(1)

Table 2. 2,4,6-Trialkyl-1,3,5-triazines from unsubstituted alkyl cyanides RCN.

R	Reaction conditions				Yield, wt.%	Ref.
	10^3p, atm	T, °C	solvent	duration, h		
CH_3	7.9	120	methanol	10	29	32
	7.9	120	ethanol	10	6	32
	7.9	120	ethanol	24	11	32
C_2H_5	7.9	120	ethanol	24	7	32
	7—8	70	methanol	65	36	30, 31
C_3H_7	7.9	120	ethanol	24	1	32
n-C_4H_9	7—8	150	methanol	18	35	30, 31
	7—8	100	methanol	18	7	30, 31
t-C_4H_9*	10.5	130	thiolan *S*-dioxide	8	50	33
	9	160	thiolan *S*-dioxide	6	90	33
	8—9	200—210	ethanol	10—15	90	33
	8—9	200—210	propan-1-ol	10—15	70	33

*Methanol used as catalyst.

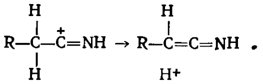
Such rearrangements have been observed[33] even in the absence of amines, under 9000 atm at 200°C. They were explained by the scheme



(2)

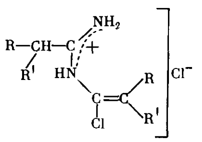
As evidence of the formation of an intermediate imidic ester 2-substituted benzimidazoles were isolated[33] on the addition of *o*-phenylenediamine to the reaction mixture. 4-Aminopyrimidines may be formed either through an intermediate stage from 1,3,5-triazines (schemes 1 and 2) or directly from the initial compounds. They were not observed[34] in the acid-catalysed formation of 1,3,5-triazines from imidic esters.

Several attempts have been made to synthesise 1,3,5-triazines by the cyclotrimerisation of unsubstituted alkyl cyanides in the presence of acids, but this has not yet been achieved. Ruske[35] explains the lack of success by the hyperconjugation effect of the alkyl radical, which diminishes the electrophilic character of the cyanide carbon atom and thus hinders addition of the next cyanide molecule:



$$R{-}\underset{H}{\overset{H}{C}}{-}\overset{+}{C}{=}NH \rightarrow R{-}\underset{H^+}{\overset{H}{C}}{=}C{=}NH\ .$$

Yanagida et al.[36] have also investigated the reaction between alkyl cyanides and hydrogen chloride, and have shown that stable hydrochlorides of *N*-substituted amidines



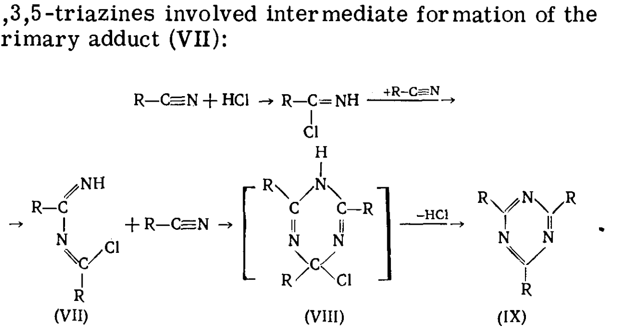
(VI)

are formed. The use of Lewis acids as catalysts for the cyclotrimerisation of acetonitrile also failed to yield the corresponding 1,3,5-triazine: 4-amino-2,6-dimethylpyrimidine was isolated[37].

2. 2,4,6-Trialkyl-1,3,5-triazines from Substituted Alkyl Cyanides

1,3,5-Triazines are formed from α-halogenated alkyl cyanides by acid catalysis, since the hyperconjugation effect of the α-carbon–hydrogen bond is counteracted by the effect of the substituent. Thus, whereas monohalogenated acetonitriles do not usually trimerise‡, and dihalogenated acetonitriles trimerise with insignificant yields§, trihalogenated acetonitriles readily yield the corresponding 2,4,6-tristrihalogenomethyl-1,3,5-triazines.

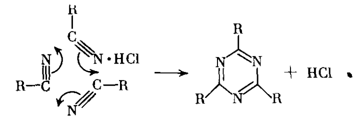
In the presence of hydrogen chloride the catalytic process leads to formation of a primary adduct[36,38,39] of the type 2RCN.3HCl. The electrophilicity of dimers of monohalogenoacetonitriles then becomes weaker in comparison with the monomer, and addition of another nitrile molecule impossible[40]. The mechanism first suggested[40] for this acid-catalysed cyclotrimerisation of $\alpha\alpha$-di- and $\alpha\alpha\alpha$-tri-halogenated alkyl cyanides to the corresponding 1,3,5-triazines involved intermediate formation of the primary adduct (VII):



(3)

This was followed[40] by cycloaddition of another cyanide molecule to give the 2,4,6-trialkyl-4-chloro-1,4-dihydro-1,3,5-triazine (VIII), which underwent spontaneous dehydrohalogenation to the 1,3,5-triazine (IX), However, treatment of $2CCl_3CN.HCl$ with acetonitrile does not yield the expected 1,3,5-triazine, although cyclotrimerisation of trichloroacetonitrile together with acetonitrile in the presence of hydrogen chloride gives the corresponding methylbistrichloromethyl-1,3,5-triazine[40].

Zil'berman[41,42] has suggested a different mechanism, in which the relatively easy formation of 1,3,5-triazines is due to a large gain in energy accompanying cyclisation, which may involve cyclic electron transfer:



On this view both free nitriles and their complexes with hydrogen halides take part in the formation of triazines.

Sulphuric acid[47], Lewis acids[47–49], and complexes of the latter with hydrogen halides[50–53] have also been used as acid catalysts, among which the complexes are the best for cyclotrimerisation. Zil'berman et al.[48] have described the preparation of 2,4,6-tristrichloromethyl-1,3,5-triazine from the complexes

$2Cl_3C{-}CN\cdot AlCl_3$; $Cl_3C{-}CN\cdot AlCl_3$; $Cl_3C{-}CN\cdot 2AlCl_3$.
(X) (XI) (XII)

at 100°C (Table 3). They showed[48] that raising the temperature to 140–150°C leads to the formation of polymers, hexachloroethane, and cyanogen in various proportions. Polymeric products are also formed from dichloroacetonitrile in the presence of aluminium trichloride at 100°C.[49]

A large number of possible catalysts have been reported for the cyclotrimerisation of fluorinated nitriles to 1,3,5-triazines, including metal oxides[54,55]

(Al_2O_3, Bi_2O_3, CaO, Ag_2O, Co_2O_3, Fe_2O_3, HgO, PbO_2, Cu_2O, BaO, Sb_2O_3, TiO_2, V_2O_3, Y_2O_3, ZnO, Mn_2O_3, Tl_2O_3)

silver salts[56]

(AgCl, AgBr, AgI, $AgClO_3$, $AgNO_3$, Ag_2SO_3, Ag_2SO_4, $AgClO_4$, $AgBF_4$

fluorides[56]

SnF_2, CdF_2, ThF_2, AgF, CoF_2, CoF_3, FeF_2, FeF_3, CrF_3, VF_5, CuF_2, ZnF_2, NaF, KF, NH_4F, NH_4BF_4, SnF_4, LiF, NiF_2);

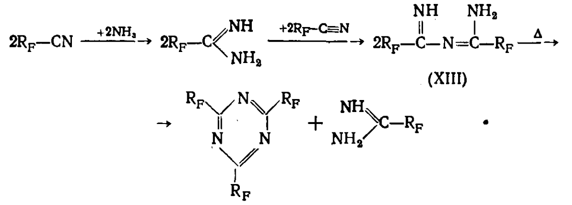
and organometallic compounds[57] [e.g. $(n\text{-}C_8H_9)_3SbO$ and $(CH_3)_3Sb(OH)_2$], as well as amine oxides[58]. Ammonia also catalyses the cyclotrimerisation of fluorinated

---

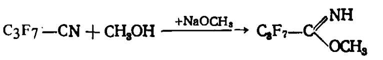
‡Yanagida et al.[36] have obtained 2,4,6-trischloromethyl-1,3,5-triazine from the adduct $2CH_2ClCN.2HCl$.

§It was assumed in the early work that dimers were formed[43–46].

nitriles $R_F.CN$¶, both at high[59] and at normal[59-62] pressures. At normal pressure the reaction is assumed to involve intermediate formation of imidoylamidines (XIII)[59,60]:

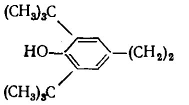
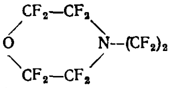

(XIII)

In the presence of alcohols at high pressures the formation of 1,3,5-triazines from fluorinated alkyl cyanides[63] and also from 1,1-dichloropropionitrile[30] may involve an imidic ester stage:


$$C_3F_7-CN + CH_3OH \xrightarrow{+NaOCH_3} C_3F_7-C\begin{matrix}{=}NH\\ {-}OCH_3\end{matrix} .$$

At 70–140 atm fluorinated alkyl cyanides trimerise even in the absence of a catalyst[62]. The uncatalysed cyclotrimerisation of pentafluoropropionitrile at normal pressure has been reported[62], providing additional

Table 3. 2,4,6-Trialkyl-1,3,5-triazines from substituted alkyl cyanides RCN.

R	Reaction conditions					Yield, wt.%	Ref.
	catalyst	*p*, atm	*T*, °C	solvent	duration, h		
$HO(CH_2)_n$ (n = 3,4,5)	Cu, Zn, Fe halides	—	0—50	—	—	—	69
$HO(CH_2)_n$ (n = 3,4,5)	—	500	0—50	—	—	—	69
$HO(CH_2)_n$ (n = 3,4,5)	$h\nu$	—	0—50	—	—	—	69
$HO(CH_2)_n$ (n = 3,4,5)	HCl	—	0	ethanol	8	73	70
	CH_3COOH	—	—	—	72	73	70
C_2H_5-O-CO [a]	HCl	—	—	—	2-4 weeks	~96	71
Cl_2HC [b]	HCl; HBr	—	—	—	—	—	43,45,46
Cl_2HC	$AlCl_3$	—	50—70	—	6	20	49
F_3C	HCl	0—0.5	—	—	18—20	—	72
CF_3	—	42—70	300	—	16	31	62
CF_3-CF_2	—	—	300	—	120	48	62
$CF_3-(CF_2)_2$	—	117—139	350—400	—	130	8	62
$CF_2Cl-CFCl$	$AlCl_3/HCl$	—	22—60	—	20	~50	74
$CF_2Cl-CFCl$	$AlCl_3/HCl$	c	100	—	16	25	74
$CF_2H-CF_2-O-(CF_2)_{;}-O-(CF_2)_2$	NH_3	—	165—175	—	20	88	61
$HCFCl-CF_2-O-(CF_2)_2$	NH_3	—	150	—	19	80	61
	NH_3	—	150	—	14	88	61
CH_3-CCl_2	HCl	—	25	—	a few months	—	75
CH_3-CCl_2	—	7000—8000	100	methanol	18	74	30,31
CH_3-CCl_2	—	7000—8000	125	butan-1-ol	18	8	30,31
CCl_3	HCl[d]	—	—10—25	—	12	2	50
CCl_3	HCl	56	—	—	100	96	76
CCl_3	HBr[e]	—	—10—25	—	12	34	50
CCl_3	H_2SO_4	—	150[f]	—	4	—	47
CCl_3	$AlCl_3$	—	100	—	12	60	48
CCl_3	AlF_3/HCl	—	—10—25	—	12	~67	50
CCl_3	$AlCl_3/HCl$	—	—10—25	—	12	~36	50
CCl_3	$AlCl_3/HCl$	—	75	—	5	~93	51
CCl_3	$AlCl_3/HCl$; $AlBr_3/HCl$	—	—40—20	—	3—20	80—93	52
CCl_3	$AlBr_3/HCl$ or HBr	—	—10—25	—	12	~95	50
CCl_3	$AlBr_3/HCl$	—	25—65	—	~4	95	51
CCl_3	BF_3-ether/HCl	—	—10—25	—	12	94	50
CCl_3	PCl_5/HCl	—	100—105	—	240	82	53
CCl_3	$FeCl_3/HCl$	—	—10—25	—	12	~44	50
CCl_3	$ZnCl_2/HCl$	—	—10—25	—	12	~42	50
CCl_3	$SnCl_4/HCl$	—	—10—25	—	12	~52	50
CCl_3	$SnCl_3/HCl$	—	—10—25	—	12	~47	50
CCl_3	$TiCl_4/HCl$	—	—10—25	—	12	~41	50
CCl_3	$TiBr_4/HCl$	—	—10—25	—	12	~62	50
CBr_3	HCl	—	—	—	a few days		76,77,80

[a] See also Refs. 40 and 73.

[b] Formation of polymers favoured by raising the temperature to 100–130°C and also by high concentration of aluminium chloride.

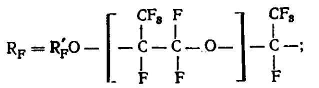
[c] Reaction conducted in an autoclave.

[d] See also Refs. 73, 77, and 78.

[e] See also Refs. 43, 77, and 79.

[f] Below 80°C the main reaction product is $(CCl_3CONH_2)_2SO_2$.

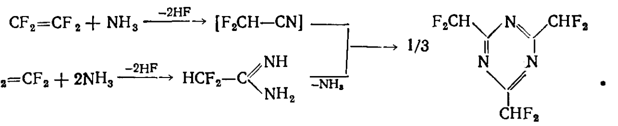
¶ Here


$$R_F = R'_FO-\left[-\underset{F}{\overset{CF_3}{C}}-\underset{F}{\overset{F}{C}}-O-\right]-\underset{F}{\overset{CF_3}{C}}-;$$

R'_F = CF_3, $Hal[CF_2]_m$, $H[CF_2]_m$, where m = 1–8, n = 1–20, T = 300–350°C, and p = 49–63 atm.

evidence of the highly electrophilic character of the nitrile group in perfluorinated alkyl cyanides.

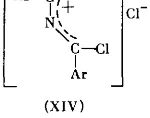
Syntheses of 1,3,5-triazines have also been described[63-67] in which halogenated nitriles are probably intermediate products. Thus the action of chlorine on acetonitrile and on propionitrile yields 2,4,6-tristrichloromethyl- and 2,4,6-trisdichloroethyl-1,3,5-triazine respectively[65-67]. A fluorinated triazine has been obtained[64] via an intermediate amidine stage:



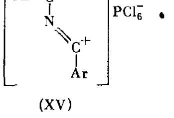
The action of chlorine or bromine on 1,2,2,2-tetrafluoroethyl cyanide gives 2,4,6-tris-1′-chloro(or bromo)tetrafluoroethyl-1,3,5-triazine[68].

IV. 2,4,6-TRIARYL-1,3,5-TRIAZINES FROM ARYL CYANIDES

2,4,6-Triphenyl-1,3,5-triazine (cyaphenine) was first isolated[81] from the reaction between benzoyl chloride and potassium cyanide. It was first obtained by the cyclotrimerisation of benzonitrile in the presence of metallic sodium in 1868.[82] Later, in 1878, a method of synthesising 2,4,6-triaryl-1,3,5-triazines was developed[83] by the acid-catalysed cyclotrimerisation of aromatic nitriles, a process which has since been widely used. Good yields of 2,4,6-triphenyl-1,3,5-triazines are obtained by using as catalyst chlorosulphuric acid[84] in the molecular proportions $HSO_3Cl : C_6H_5CN = 3 : 1$ at 0°C. Increasing this ratio or lowering the temperature diminishes the yield. Raising the temperature by 10 deg also lowers the yield of trimer as a consequence of sulphonation of the benzonitrile. Hydrogen chloride is a weak cyclotrimerisation catalyst, since it forms a stable 2 : 2 adduct with benzonitrile[39], but when a Lewis acid is also present high yields of triaryltriazines are formed[53,85]. It was assumed[53] that the mechanism of formation of triphenyltriazine in this case consisted in weakening of the nucleophilic character of the chloride ion in the adduct (XIV) by formation of the complex (XV) with the Lewis acid (phosphorus pentachloride):



(XIV)

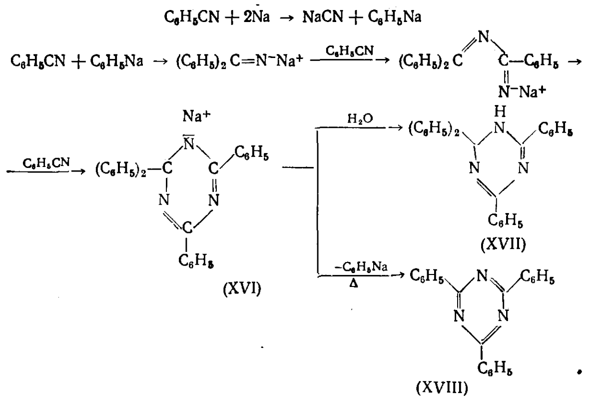


(XV)

The hexachlorophosphate (XV) reacts further with another molecule of the aryl cyanide or with an adduct (1 : 1) of the nitrile and phosphorus pentachloride to give a 1,3,5,triazine, which may also be formed[39] by the pyrolysis of (XIV).

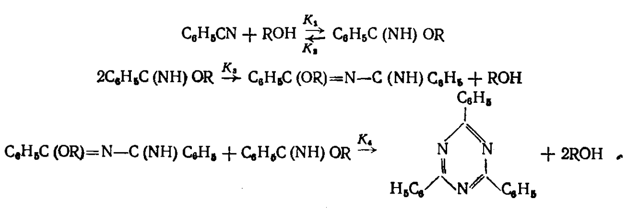
Lewis acids—aluminium, phosphorus(V), zinc, and titanium(IV) chlorides and boron trifluoride—have been used as catalysts for the cyclotrimerisation of aryl cyanides[50,53,86-91]. Their catalytic activity is considerably lower than that of corresponding mixtures of Lewis acids with various promoters—proton-containing compounds (mineral acids, water, amides, organic acids) and organic compounds containing mobile halogens—e.g. benzoyl chloride, etc.[87-89] Such a difference in catalytic activity is attributed to a change in the structure of the complexes† of the aryl cyanides with the Lewis acids[6,92-94]. When complexes of benzonitrile with Lewis acids are heated, either triphenyltriazine or a linear polymer of azomethine structure may be obtained depending on the conditions chosen (temperature, nature of complexes, additions of promoters, etc.)[87-89,92,95]. Pure Lewis acids have little catalytic effect on the cyclotrimerisation of nitriles[50], and only additions of cocatalysts (water, hydrogen chloride, etc.) produce a marked increase in their activity (see below).

The reactions involved in the trimerisation of benzonitrile in the presence of bases have been studied in detail[97-100]. The action of sodium on benzonitrile forms initially phenylsodium‡, to which three molecules of benzonitrile then add successively to give the sodium salt of 1,2-dihydro-2,2,4,6-tetraphenyl-1,3,5-triazine (XVI):



Hydrolysis of (XVI) gives the dihydro-1,3,5-triazine (XVII) in 85% yield[100]. When (XVI) was heated in a high-boiling solvent (xylene or nitrobenzene), 2,4,6-triphenyl-1,3,5-triazine (XVIII) was isolated[99]. The elimination of phenylsodium is accelerated by passing carbon or sulphur dioxide through the reaction mixture or by adding benzonitrile.

The cyclotrimerisation of aryl[30,31,33,43] and heterocyclic[33] cyanides catalysed by amines and alcohols under high pressures occurs similarly to that of alkyl cyanides described above. The trimerisation of benzonitrile in the presence of an alcohol under 2–10 kbar at 100–120°C involves initial formation of the benimidic ester[101]:



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†For the structure of the complexes of nitriles with Lewis acids see also Ref. 96, pp. 571 and 583.

‡With organic compounds of alkali metals of the type RCH_2Na 2,4,6-triphenylpyrimidine is formed (with elimination of ammonia)[98].

Raising the pressure shifts the equilibrium towards formation of the trimer, whereas increasing the chain length and the degree of α-branching of the alcoholic radical hinders this reaction:

$CH_3OH > C_2H_5OH \approx n\text{-}C_3H_7OH \approx n\text{-}C_4H_9OH > iso\text{-}C_3H_7OH \approx s\text{-}C_4H_9OH.$

The reaction is second order with respect to the imidic ester: i.e. dimerisation (K_3) is the rate-determining stage. Polar solvents accelerate the reaction and increase the yield of trimer. The reaction is completely suppressed by acids; bases have hardly any effect. The effects of acid and basic catalysts on cyclotrimerisation are fundamentally different at high and normal pressures: in the latter case the reaction occurs in the presence of strong acids or bases. Raney nickel[102] and iron carbonyls[103] are relatively weak catalysts for the trimerisation of aryl cyanides.

Even in the absence of a catalyst aryl[30,31,104] and also heterocyclic[33] cyanides can be trimerised at high pressures. Formation of a dipolar intermediate form $R\text{-}C^{+}{=}N^{-}$ can be assumed, since in dipolar aprotic solvents[104], e.g. thiolan *S*-dioxide, trimerisation occurs under milder conditions than in the absence of a solvent[105].

Table 4. 2,4,6-Triaryl-1,3,5-triazines from aryl cyanides RCN.

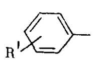
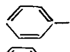
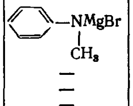
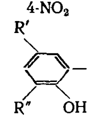
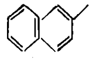
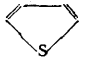
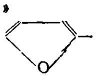
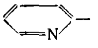
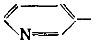
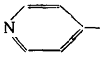
R	Reaction conditions					Yield, wt.%	Ref.
	catalyst	$10^{-3}p$, atm	T, °C	solvent	duration, h		
							
R′=H	HCl	—	100—105	—	—	trace	53
H	HCl	—	—	ethanol	24—48	—	106
H	H_2SO_4	—	—	—	24	—	83
H	HSO_3Cl	—	0	—	12	40	107
H	HSO_3Cl	—	0—5	—	12—24	~88	84
H	$AlCl_3$	—	140—160	—	6	—	86
H	PCl_5	—	~100	—	240	40	53
H	PCl_5/HCl; PBr_5/HCl; $SbCl_5/HCl$	—	100	—	24	98	85
H	PCl_5/HCl	—	100—105	—	24	98	53
H	$SbCl_5/HCl$ *	—	100—105	—	24	62	53
H	PBr_5/HCl	—	100—105	—	24	20	53
H	$AlCl_3/HCl$	—	100—105	—	24	18	53
H	$SnCl_4/HCl$	—	100—105	—	24	21	53
H	$FeCl_3/HCl$; $ZnCl_2/HCl$	—	100—105	—	24	13	53
H	Na **, CO_2 or SO_2	—	80	benzene, xylene	27	~23	100
H	NaH	—	70—85	benzene, nitrobenzene, xylene	—	14	99
H	NaH	—	70—200	benzene, nitrobenzene	~6	14	99
H	—NHNa	—	35—190	ether	2	12	99
H	 $C_6H_5N(CH_3)MgBr$	—	142	n-butyl ether	12	~21	99
H	—	—	285	pyrrolid-2-one	8	41	108
H	—	—	325	pyrrolid-2-one	8	44	108
H	—	7.5	100	methanol	18	76	30,31
H	—	7.5	125	methanol	18	82	30,31
H	—	7.5	100	ethanol	18	24	30,31
H	—	7.5	150	propan-2-ol	18	46	30,31
H	—	7.5	125	ethylhexanol	18	22	30,31
H	—	8—10	200	methanol	—	95	33
H	—	50	430	—	6***	~100	105
H	—	35	400	—	18***	~100	105
H	—	15.8	360	—	14	2.5	105
H	—	7.5	125	—	18	6	30,31
H	$Fe(CO)_5$; $Fe_2(CO)_9$	—	~190	—	a few hours	—	103
H	Ni, CH_3COOH	—	~190	—	48	3	
4-CH_3O	PCl_5/HCl	—	~100	nitrobenzene	120	8	53
2-CH_3	HSO_3Cl	—	0	—	48	—	107

Table 4. (contd.)

R	Reaction conditions					Yield, wt.%	Ref.
	catalyst	$10^{-3}p$, atm	T, °C	solvent	duration, h		
2-CH_3	H_3PO_4	37.5	350	—	16***	100	105
2-CH_3	—	50	480	—	6***	50	105
3-CH_3	HSO_3Cl	—	0	—	12	—	105
3-CH_3	PCl_5/HCl *	—	~100	—	120	63	53
3-CH_3	—	50	545	—	7***	100	105
4-CH_3	HSO_3Cl	—	0	—	12	—	107
4-CH_3	PCl_5/HCl	—	100—105	—	90	60	105
4-CH_3	—	50	500	—	6***	~100	105
4-CH_3	—	38.5	350	—	16***	30	105
4-Cl	HSO_3Cl	—	0	—	12	—	107
2-CN	acid	—	235	—	20	45	109
3-CN	$ZnCl_2$	—	360	—	25***	100	91
3-CN	$ZnCl_2$	—	420	—	2	89	91
3-CN	$ZnCl_2$	—	275	—	4	38	90
3-CN	PCl_5	—	250	—	9	—	90
3-CN	P_2O_5	—	250	—	5	52	90
3-CN	—	—	285	pyrrolid-2-one	24	46	108
4-CN	$AlCl_3/HCl$	—	100—105	nitrobenzene	120	26	53
4-CN	PCl_5/HCl	—	100—105	nitrobenzene	120	34	53
4-CN	$ZnCl_2$	—	270	—	5	64	90
4-CN	—	—	285	pyrrolid-2-one	24	50	108
4-NO_2	$AlCl_3/HCl$	—	100—105	nitrobenzene	120	16	53
4-NO_2	PCl_5/HCl	—	100—105	nitrobenzene	120	62	53
							
R′=H, Cl, Br; R″=H	—	—	160—180	—	2—3	—	110
R′=H, R″=CN; R′=CN, R″=H	—	—	153	*NN*-dimethylaniline	1	—	111
R′=NO_2, R″=H	—	—	melt	—	—	—	112
R′, R″=Br	—	—	melt	—	—	—	112
	PCl_5/HCl *	—	100—105	nitrobenzene	120	22	53
	—	8—10	200	piperidine	—	90	33
ditto	—	8—10	200	thiolan *S*-dioxide	—	50	33
»	—	8	180	methanol	5	90	33
	—	8.2	100	methanol	5	60	33
	NaOH	—	—	—	30***	—	113
	NaOH	—	—	—	30***	25	113
	NaOH	—	—	—	30***	25	113
ditto	$SnCl_4$	$1.3\cdot10^{-6}$	320	—	—	15	114
»	$NaOC_2H_5$	****	220	ethanol	22	90	114

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*Chlorinated 1,3,5-triazines formed as byproducts.

**Phenylsodium is an active catalyst, and has been used for the cyclotrimerisation of benzonitrile.[71,80,81]

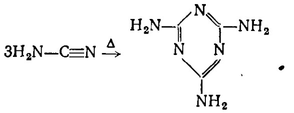
***Duration of reaction in minutes.

****Reaction conducted in an autoclave.

Steric factors also exert a strong influence on cyclotrimerisation. With *ortho*-substituted aryl cyanides, in contrast to the *meta*- and *para*-derivatives, severe conditions are required, and 1,3,5-triazines are formed from them in lower yields. 9-Cyanophenanthrene, 9-cyanoanthracene, and adamant-1-yl cyanide do not trimerise[33] even under 8000-17 000 atm at 150-240°C (Table 4).

V. 1,3,5-TRIAZINE-2,4,6-TRIAMINES (MELAMINES) FROM CYANAMIDES

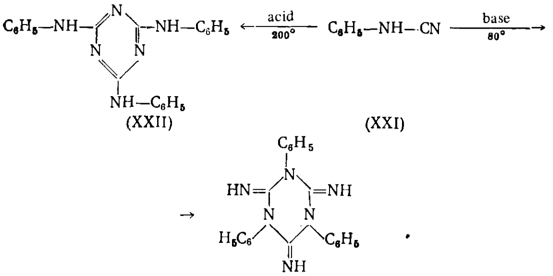
Few results have been published on the cyclotrimerisation of cyanamide (XIX) to form 1,3,5-triazine-2,4,6-triamine (XX):


(XIX) (XX)

This synthesis is achieved either in molten cyanamide above 150°C (Ref. 1, p. 309) or by heating in a solvent of high boiling point[115].

The cyclotrimerisation of substituted cyanamides has been reported repeatedly (Ref. 1, p. 349), but until recently published results were contradictory[116-122]: in some cases the products were isomelamine derivatives[116, 117, 120], whereas in others substituted melamines of normal structure were obtained[118, 119, 121, 122]. From these results it may be concluded that 1,3,5-triazine-2,4,6-triamines are formed more readily if the substituting groups cause steric hindrance to attack on the NH group, as do tertiary alkyls[118, 119, 121], adamant-1-yl,[119] and *ortho*-substituted aryls[122].

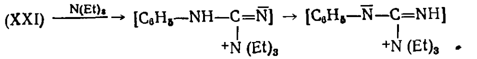
A recent series of investigations[123-128] on the cyclotrimerisation of phenylcyanamide (XXI) has shown that either the normal triphenylmelamine (XXII) or triphenylisomelamine (XXIII) may be formed depending on the conditions:


(XXII) (XXI) (XXIII)

Thus in the melt under mild conditions (20–80°C) the cyclotrimerisation of (XXI) yields (XXIII), whereas at 200°C the normal product (XXII) is mainly formed[123]. The structure of the final product is determined also by the nature of the catalyst: in the presence of Lewis acids—tin(II), zinc, titanium(IV) chlorides, etc.—(XXII) is formed, but basic catalysts—triethylamine, pyridine, triphenylphosphine, etc.—yield the iso-form (XXIII).

As in the catalytic cyclotrimerisation of nitriles, Lewis acids probably form with (XXI) adducts in which the electron pair of the π bond has been displaced to different extents, from molecular compounds of the type $C_6H_5.NH.C\equiv N, MX$ to ionic structures $C_6H_5.NH.C^+:N.M^-X$. Increasing the polarisation of the cyano-groups tends to accelerate the cyclotrimerisation of (XXI) to (XXII).

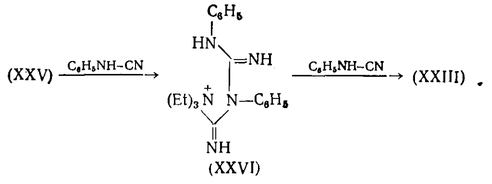
Catalysis by triethylamine probably involves formation of a complex with (XXI) by nucleophilic attack by the nitrogen atom of the tertiary amine on the electrophilic carbon atom of the nitrile group:



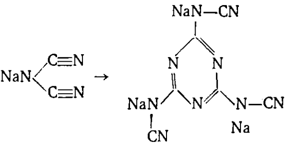
$$(\mathrm{XXI}) \xrightarrow{N(Et)_3} [C_6H_5-NH-\underset{+N(Et)_3}{C}=\bar{N}] \rightarrow [C_6H_5-\bar{N}-\underset{+N(Et)_3}{C}=NH] \;.$$

(XXIV) (XXV)

It is probable that (XXV) is more stable than the tautomeric structure (XXIV). This is supported by infrared spectroscopy, since addition of triethylamine to a toluene solution of (XXI) is accompanied by weakening in the spectrum of the mixture of the absorption band at 2230 cm^{-1} characteristic of vibrations of the N≡C bond in cyanamides,[129] with appearance of a band at 2130 cm^{-1} due to vibrations of the carbodi-imide group[129]. The complex (XXV) evidently then adds two more (XXI) molecules to form triphenylisomelamine (XXIII) via the transition state (XXVI)[125]:


(XXVI)

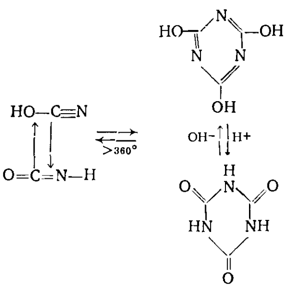
The trimerisation of disubstituted cyanamides was first described by Weith[130], who obtained hexaphenylmelamine by the action of cyanogen chloride on diphenylamine, which should involve intermediate formation of diphenylcyanamide. 2,4,6-Tripyrrol-1′-yl-1,3,5-triazine was also obtained by the action of cyanogen chloride on pyrrole.[131] Heating the sodium salt of dicyanamide gave the trisodium salt of 2,4,6-triscyanoamido-1,3,5-triazine[132]:



A kinetic study of the cyclotrimerisation of *N*-ethyl-*N*-phenylcyanamide has shown[126] that the presence of an aliphatic substituent α to the cyano-group diminishes the reactivity of the cyanamide group, so that this compound cyclotrimerises only in the presence of a cationic catalyst such as a Lewis acid to form 2,4,6-tris-(*N*-ethyl-*N*-phenylamino)-1,3,5-triazine. The presence of an isomelamine structure among the reaction products was not detected[126].

VI. CYANURIC ACID FROM CYANIC ACID

Cyanic acid exists in tautomeric equilibrium with isocyanic acid, and hence two forms of its trimers are possible—enolic (XXVII) and ketonic (XXVIII):


(XXVII)

(XXVIII)

Polymerisation of cyanic acid yields not only cyanuric acid but also cyamelide,[133-135] a polymer (or trimer) of cyanic acid in which the carbonyl bond has been opened. Cyamelide is an amorphous white powder, insoluble in water and organic solvents, and readily depolymerised when heated (especially in the presence of acids). The polymerisation of cyanic acid vapour above 150°C results in formation mainly of cyamelide, but below this temperature the chief product is cyanuric acid[135], which depolymerises at about 360°C.

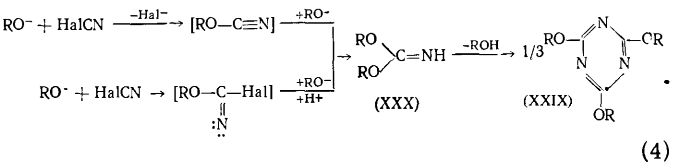
The Raman spectra show that solid cyanuric acid is present in the keto-form[136], which is confirmed by numerous investigations of the infrared spectra[137–140]. In solution the content of a particular form is determined by the pH: thus in saturated aqueous solution[141] at 20°C the content of the enolic form is 5.6%, in strongly alkaline medium the trimer is present in the enolic form, but in acid medium (pH < 6) the keto-form predominates[142–144]. An explanation of the predominance of the keto-form of cyanuric acid in neutral solution and in the solid state is that the loss of π–π conjugation is largely balanced by strong n–π conjugation, which makes this form the energetically more favourable structure.

Several syntheses of cyanuric acid other than the cyclotrimerisation of cyanic acid have been described[1,135] (see Ref. 2, p. 26). The principal industrial method is the pyrolysis of urea:

$$3NH_2CONH_2 \rightarrow (HOCN)_3 + 3NH_3 \ .$$

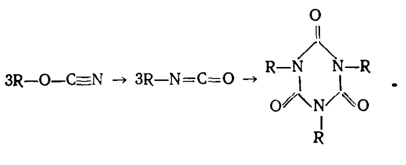
VII. 2,4,6-TRIALKOXY-1,3,5-TRIAZINES (TRIALKYL CYANURATES) FROM ALKYL CYANATES

Trialkyl cyanurates (XXIX) were first obtained in attempts to prepare alkyl cyanates from alkoxides and cyanogen halides[145–148]. A carbonimidic ester (XXX) is an intermediate product, which Nef[149] assumed to be formed directly from the anion of the chloroformidic ester, whereas other workers[150] assumed initial formation of the alkyl cyanate:



(4)

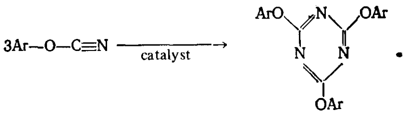
An obstacle to direct trimerisation of alkyl cyanates is the lability of the alkyl–oxygen bond, which results in side reactions. Thus the nucleophilic catalysts and anions of Brønsted acids used for trimerisation undergo alkylation[151,152], whereas Lewis acids and exposure to light of wavelength ≤250 nm promote their isomerisation into alkyl isocyanates[153]. Even on attempted distillation at normal pressure or on heating in solvents alkyl cyanates are isomerised into isocyanates[154–157], which in turn partly trimerise to form isocyanurates:



The rate of this isomerisation depends on the polarity of the solvent and on its ability to solvate cations. Solvents investigated in relation to this reaction form the sequence toluene < nitrobenzene ≈ acetonitrile < dimethylformamide ≪ dimethyl sulphoxide according to their tendency to isomerise alkyl cyanates[158]. Steric hindrance or strongly electron-accepting substituents enhance the stability of alkyl cyanates[7,158–164]. Thus 2,2,3,3-tetrafluoropropyl cyanate has been cyclotrimerised in theoretical yield to the corresponding cyanurate[159,160]. Carbaborane-containing cyanic esters $CB_{10}H_{10}CCH_2.O.C{\equiv}N$ resistant to isomerisation have been obtained[7,161–163], which also undergo selective trimerisation to the corresponding cyanurate structures[7,162,164].

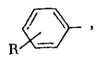
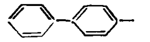
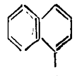
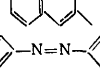
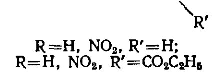
VIII. 2,4,6-TRIARYLOXY-1,3,5-TRIAZINES (TRIARYL CYANURATES) FROM ARYL CYANATES

In the presence of catalysts aryl cyanates readily undergo trimerisation to 2,4,6-triaryloxy-1,3,5-triazines (Table 5):



In contrast to alkyl cyanates, aryl cyanates do not isomerise into isocyanates: resonance interaction occurs between the cyanato-oxygen atom and the aromatic ring[165] (σ_R^0 = −0.27), which stabilises the carbon–oxygen bond.

Table 5. 2,4,6-Triaryloxy-1,3,5-triazines from aryl cyanates ArOCN.

Ar	Reaction conditions				Yield, wt.%	Ref.
	catalyst	*T*, °C	solvent	duration, h		
						
R=H	$NaOC_2H_5$; $ZnCl_2$	200	—	2—5*	85	157
H	PCl_5	20	CCl_4	~2	95	165
2-CH_3	PCl_5	20	CCl_4	~2	95	165
3-CH_3	PCl_5	20	CCl_4	~2	15	165
4-CH_3	$NaOC_2H_5$; $ZnCl_2$	200	—	2—5*	84	157
4-CH_3	$AlCl_3$	50—60	—	~5*	100	158
4-CH_3	HCl(gas)	—	ether	—	100	158
4-CH_3O	$NaOC_2H_5$; $ZnCl_2$	200	—	2—5*	98	157
4-Cl	$NaOC_2H_5$; $ZnCl_2$	200	—	2—5*	80	157
4-Cl	PCl_5	20	CCl_4	~2	35	165
2-Br; 4-Br	PCl_5	20	CCl_4	~2	30	165
	$AlCl_3$	150	—	—	80	159
	PCl_5	20	CCl_4	~2	65	165
	PCl_5	20	CCl_4	~2	95	165
 R=H, NO_2, R′=H; R=H, NO_2, R′=$CO_2C_2H_5$	$AlCl_3$	—	—	—	—	166

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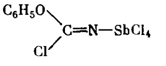
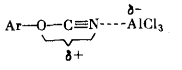
*Duration of reaction in minutes (Ed.of Translation).

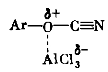
Active catalysts for the trimerisation of aryl cyanates include protic and aprotic acids[7,158,166–180] and bases[157,166–168,173,175–181], mixtures thereof[176], transition-metal complexes[176–178,182–190], and others[176]. Several hypotheses on the mechanism of catalysis of this reaction by Lewis acids [antimony(V), tin(IV) and aluminium(III) chlorides, the ether complex of boron trifluoride] were made by Martin and Weiss[172] in an infrared spectroscopic investigation of complexes of aryl cyanates with Lewis acids. But, whereas the boron trifluoride–ether complex produces no change in the structure of phenyl cyanate, antimony pentachloride forms in dichloromethane solution the complex (XXXI). From the shift in the infrared absorption band of the cyanato-group and the appearance of a few new bands in the range 1700–700 cm^{-1} it was suggested that structures such as (XXXII)–(XXXVI) might be formed. Structure (XXXVII) was assumed for the complex $ArOCN-SnCl_4$. The way in which the complexes (XXXII)–(XXXVII) are involved in trimerisation has not yet been ascertained[172].



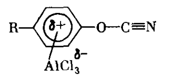
(XXXI)



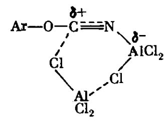
(XXXII)



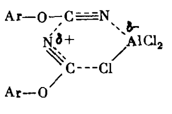
(XXXIII)



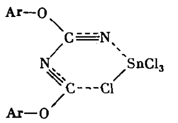
(XXXIV)



(XXXV)

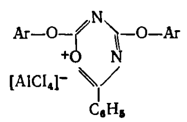


(XXXVI)



(XXXVII)

The complex of aluminium and benzoyl chlorides[174] causes especially rapid trimerisation of aryl cyanates, probably with intermediate formation of 2,4-diaryloxy-6-phenyl-3,5-diazapyrylium tetrachloroaluminate[191]



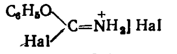
This intermediate can be isolated by replacing aluminium(III) by antimony(V) chloride.

Shevchenko et al.[170] trimerised aryl cyanates in the presence of phosphorus pentachloride, and showed that the reactions

$$ArO{-}C{\equiv}N + PCl_5 \rightarrow ArO{-}C(Cl){=}N(PCl_4) \xrightarrow{+PCl_5}$$
$$\rightarrow [ArO{-}C(Cl){=}N(PCl_3)]^+PCl_6^- \xrightarrow{+ArO-C\equiv N} [(ArOC(Cl){=}N)_2PCl_2]^+PCl_6^-$$

occurred between −20 and −40°C.

Gaseous hydrogen chloride is a very good catalyst for the trimerisation of aryl cyanates[158,173–175]. On cooling in inert solvents phenyl cyanate forms with excess of anhydrous hydrogen chloride or bromide the complex



(XXXVIII)

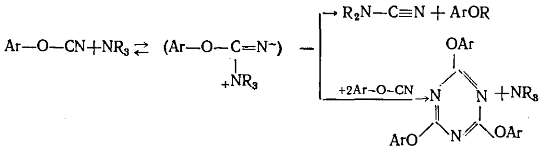
a : Hal=Cl
b : Hal=Br

which separates from solution (in almost theoretical yield). The complex (XXXVIIIa) is more stable than (XXXVIIIb), comparable in stability with the cyanamide complex $H_2NCN.2HCl$,[192] whereas the corresponding complexes of acetonitrile[173] and thiocyanates[193] decompose at room temperature§. Mesomeric interaction of the aryloxy-group with the C_{sp^2} atom obviously enhances the activity of the imino-nitrogen atom.

There are hints in the literature[176–178] that the rate of the catalytic cyclotrimerisation of aryl cyanates by Lewis acids is appreciably increased by the addition of water.

Monohydric and dihydric phenols of varying acidity have also been examined as catalysts for the trimerisation of aromatic cyanic esters. The reaction velocity increases in proportion to the decrease in the pK_a of the phenols, and appropriate correlations have been derived[176,177].

High yields of aryl cyanurates have been obtained in the presence of bases. In addition to the catalysts listed in Table 5 alkoxides[166–168], aliphatic and heterocyclic tertiary amines[166,175–178,180], and sodium hydroxide[166,175] have been used. Several suggestions have been made concerning the mechanism of trimerisation catalysed by tertiary amines[166,173,176,177,181]. Thus it has been assumed[181] that the complex (XXXIX) is formed, and then may either take part in trimerisation or break down into a cyanamide and an ether by the van Braun reaction:



(XXXIX)

Pankratov et al. have shown[195] that the substituted cyanamide is not the active catalyst in the cyclotrimerisation of aryl cyanates. With tertiary amines of type NR_3 weakening their basicity produces some decrease in rate of cyclisation[176,177]. Pyridine and isoquinoline, however, despite their weak basicity, possess catalytic activity exceeding severalfold that of the considerably more basic aliphatic tertiary amines. This phenomenon is attributed[176,177] to the greater steric accessibility of the nitrogen atom in heterocyclic amines. It is noteworthy that mixtures of trihexylamine both with diphenylpropanediol and with tin dichloride exhibit a synergistic effect when used as catalysts[176,177].

Complexes of transition metals have also been used as trimerisation catalysts[176–178,182–190]. The kinetics and the heat of cyclotrimerisation of various aryl cyanates in the presence of chromium(III) acetylacetonate have been investigated by means of a double calorimeter[182–189]. The heat of reaction, the rate, and the effective activation energy were shown to be largely determined by the nature of the solvent, and the role of specific solvation in various solvents is discussed[186]. The nature of ring substituents in phenyl cyanates also has a great influence on the heat of reaction and the kinetic parameters: electron-donor substituents diminish, whereas electron-acceptor substituents increase, the rate of cyclotrimerisation, which correlates well with the σ_R^0 constants of the substituents[187].

The trimerisation of aryl cyanates by chromium(III) acetylacetonate is autocatalytic. Investigation of the nature of the active centre has shown[185] that the presence of water accelerates cyclotrimerisation, whereas the

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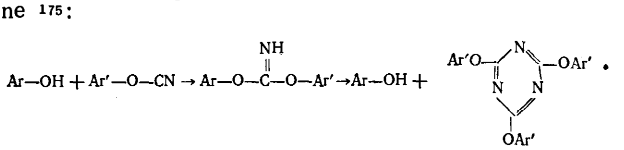
§Phenyl thiocyanate in ether does not form complexes with hydrogen chloride even at −78°C.[194]

introduction of pentane-2,4-dione considerably retards it. It was suggested that water was involved in producing the active form of the catalyst, which was in equilibrium with the main form:

$$\mathrm{Cr\,(acac)_3 + H_2O \rightleftarrows [Cr\,(acac)_2]^+OH^- + acacH}\ .$$

The 1,3,5-triazine ring is stabilised both by delocalisation of electrons to form an analogue to the π system of the benzene ring and by partial polarisation of the cyclic nitrogen–carbon bond[182,196]. The experimental heat of cyclotrimerisation of phenyl cyanate to triphenyl cyanurate was compared with the heat of reaction in the gaseous state (ΔH = −84.3 ± 1.0 and −58.2 kcal mole^{-1}). The latter value was calculated from the heats of formation of the two compounds computed additively from the contributions by the appropriate groups ($\Delta H^\circ_{\mathrm{form}}$ = 29.7 and 30.9 kcal mole^{-1}). The difference of 26 kcal mole^{-1} between experimental and theoretical heats of trimerisation was regarded as the energy of stabilisation of the 1,3,5-triazine ring (that of the benzene molecule is ~36 kcal mole^{-1}).[182,196]

Phenols add readily to aryl cyanates in the presence of bases[175] to form carbonimidic esters (XL) that decompose when heated, with separation of the more acidic phenol ($\mathrm{p}K_{\mathrm{ArOH}} < \mathrm{p}K_{\mathrm{Ar'OH}}$) and the 2,4,6-triaryloxy-1,3,5-triazine[175]:



(XL)

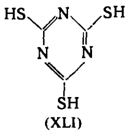
Formation of carbonimidic esters as intermediate products has been observed also in the trimerisation of aryl cyanates catalysed by alkoxides[197-201].

2,4,6-Triaryloxy-1,3,5-triazines can be formed also from aryl thiocarbamates by elimination of hydrogen sulphide followed by rapid trimerisation of the resulting aryl cyanates[169,199].

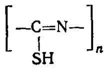
The formation of 2,4,6-triphenoxy-1,3,5-triazine from cyanogen chloride and sodium phenoxide[148,150,202] probably occurs by a similar mechanism to scheme (4).

IX. 1,3,5-TRIAZINES FROM THIOCYANIC ACID AND ITS DERIVATIVES

Thiocyanic acid exists in tautomeric equilibrium with isothiocyanic acid. In aqueous solution the equilibrium is strongly displaced towards thiocyanic acid[203], which can be trimerised to 1,3,5-triazine-2,4,6-trithiol (XLI). Only one case has yet been found[204] in which the thiocyanic acid formed in a reaction has been 23% converted into (XLI) and 77% into a linear polymer (XLII).

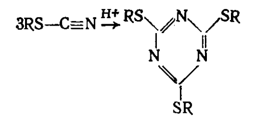


(XLI)



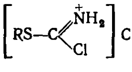
(XLII)

In contrast to alkyl cyanates, alkyl thiocyanates trimerise in the presence of acid catalysts to 2,4,6-trialkylthio-1,3,5-triazines (Ref. 1, p. 111), without formation of thio-compounds analogous to isocyanurates (Section VII)[205-207]:

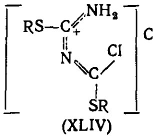


$R = CH_3,\ C_2H_5,\ C_2H_5O_2C{-}CH_2,\ CH_3{-}CO{-}CH_2$.

When heated in the absence of a catalyst, pure methyl thiocyanate does not trimerise, but isomerises into methyl isothiocyanate[205].



(XLIII)



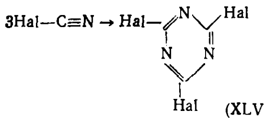
(XLIV)

Alkyl thiocyanates form adducts from hydrogen halides[39,194]. Those with two molecules of the latter (XLIII) resemble the corresponding adducts of acetonitrile[193] in being unstable at room temperature[194]. Adducts of structure (XLIV) have since been obtained[39] on the introduction of hydrogen chloride into alkyl thiocyanates (RSCN, where R = CH_3, C_2H_5, C_3H_7, C_4H_9, C_8H_{17}, $C_6H_5CH_2$); when heated, they were converted into the corresponding 1,3,5-triazines.

Trimerisation of aryl thiocyanates has not been reported: they have been used solely as "dienophiles" in mixed trimerisation (Section XI).

X. 2,4,6-TRIHALOGENO-1,3,5-TRIAZINES (CYANURIC HALIDES) FROM CYANOGEN HALIDES

Many studies have been made of the trimerisation of cyanogen halides to 2,4,6-trihalogeno-1,3,5-triazines (XLV):

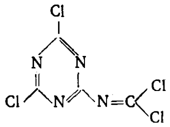


(XLV)

a) Hal = F; b) Hal = Cl; c) Hal = Br .

The more reactive the cyanogen halide, the more readily does it trimerise and polymerise: whereas liquid cyanogen fluoride is rapidly converted into (XLVa) and a polymer even at room temperature[208], trimerisation of the chloride[209-231] and the bromide[232-234] requires the presence of catalysts (acids, metal oxides or sulphides, activated carbon, zeolites, etc.). Trimerisation of cyanogen iodide has not been reported.

Together with the trimer (XLVb) have been isolated tetramers



(XLVI)

and polymers[209-212]. In some cases[209,211] the compound (XLVI) is the main product. It can be converted into (XLV) by being heated with activated carbon to 400 to 450°C.[213]

Most of the investigations on the trimerisation of cyanogen halides have been made on the chloride. Little research has been done on the mechanism of the reaction catalysed by hydrogen chloride and by Lewis acids [aluminium chloride, boron, tin(IV), and phosphorus(V) fluorides] [209–211,214–219,231,234]. Catalysis with hydrogen chloride involves initial formation of an adduct with cyanogen chloride[¶], which is then converted into a dimer. The latter reacts further either with another molecule of cyanogen chloride to give the trimer (XLVb) or with another dimer molecule to form the tetramer (XLVI).[209,210]

Good yields of (XLVb) have been obtained by using as catalysts metal sulphides and oxides,[212,220–222] activated carbon,[220–228] and also zeolites.[229,230] The catalyst poisoning that occurs with activated carbons can be diminished by introducing into them china, graphite, or quartz.[224]

Malinin et al.[216,218,223] have investigated the kinetics of the trimerisation of cyanogen chloride in the gas phase[†] on activated carbon at 280–540°C, and have found that the reverse reaction takes place above 430°C. They have suggested[218,223] a kinetic model for the range 440–540°C that takes into account the reverse reaction, the decrease in catalytic activity with time, and also the observed reaction velocities:

$$A + [K] \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} [AK] \tag{5.1}$$

$$[AK] \underset{k_{-2}}{\overset{k_2}{\rightleftarrows}} [AK^*] \tag{5.2}$$

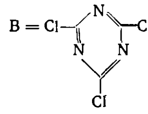
$$2[AK^*] \underset{k_{-3}}{\overset{k_3}{\rightleftarrows}} [2AK^*] + [K] \tag{5.3}$$

$$[2AK^*] + [AK^*] \underset{k_{-4}}{\overset{k_4}{\rightleftarrows}} [3AK^*] + [K] \tag{5.4}$$

$$[3AK^*] \underset{k_{-5}}{\overset{k_5}{\rightleftarrows}} B + [K] \tag{5.5}$$

$$[AK] \xrightarrow{k_6} [AK^{**}] \tag{5.6}$$

A = ClCN; B =



, [K] = Catalyst.

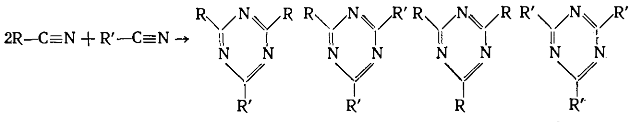
In the first stage (5.1) a molecule of cyanogen chloride is sorbed on the activated carbon, the product is activated [AK*] (5.2), and then other molecules of cyanogen chloride are added (5.3 and 5.4). After this the trimer is desorbed, and the active catalyst [K] returns to the reaction (5.5). Equation (5.6) represents the case in which cyanogen chloride does not trimerise but forms polymers $(ClCN)_n$, where $n > 3$. The trimerisation of cyanogen chloride on highly active carbons is apparently due to the presence of a graphite phase, on which cyanogen chloride molecules can be spatially oriented[229].

Wolf and Renger[229,230] have examined the influence of additions of crystalline molecular sieves on the trimerisation of cyanogen chloride. Coordination of the chloride molecules on the oxygen atoms of the catalyst facilitates their subsequent interaction to form the 1,3,5-triazine ring. The trimerisation of cyanogen chloride is a first-order reaction[229] with an activation energy of 15.2 kcal mole^{-1}.

Cyanuric halides (XLV) can be obtained not only from cyanogen halides but also directly from the halogens and hydrogen cyanide without intermediate isolation of the cyanogen halides[214,215,217,232,234].

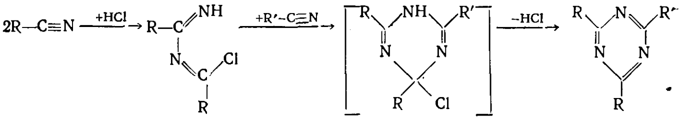
XI. MIXED CYCLOTRIMERISATION

The mixed trimerisation of two or three compounds containing a cyano-group can yield theoretically four or ten different 1,3,5-triazines. Only the former case



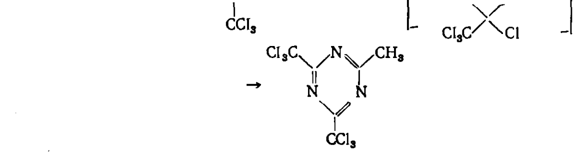
(XLVII) (XLVIII) (XLIX) (L)

has been investigated experimentally (Table 6). The catalytic activity of Brønsted and Lewis acids towards this reaction increases in the sequence from gaseous hydrogen chloride[40,50,237–243] through hydrogen chloride plus a Lewis acid to hydrogen chloride plus aluminium bromide[50,244]. In general aluminium bromide is a relatively inactive catalyst[50]. Grundmann[40] showed that catalysis by hydrogen chloride is accompanied by selective mixed trimerisation by dienophilic addition of the cyanide RCN to the adduct (LI) to form the trimer (XLVII):



(LI) (LII) (XLVII)

The intermediate complex (LII) evolves hydrogen chloride spontaneously with the formation of (XLVII). Successful selective mixed trimerisation to (XLVII) depends on the ability of the cyanides to form "dienes" (LI) and on the relative "dienophilic" activities of RCN and R'CN. When RCN forms a "diene", the products (XLVII) and (XLIX) may be expected. If the rate of addition of R'CN to the "diene" far exceeds that of RCN, the product (XLVII) is formed selectively. This occurs in the reactions of trichloroacetonitrile, catalysed by hydrogen chloride, with acetonitrile,[40,50] aryl cyanides,[40,242] and thiocyanates [50][‡] (Table 6, No. 2, 4, and 5). In the catalysed reaction between trichloroacetonitrile and acetonitrile (2 : 1) more rapid conversion is obtained[50] by using an equimolecular mixture of the ready prepared "diene" (LI) (R = CCl_3) and the equimolecular adduct of acetonitrile with hydrogen chloride instead of "free" acetonitrile:



[¶] Hydrogen fluoride acts on cyanogen halides in the absence of moisture at 200–450°C to form bistrifluoromethylamine $(CF_3)_2NH$.[235]

[†] Humphries and Nicholson[236] calculated the heat of formation of (XLVb) as 72.9 kcal mole^{-1} from the reaction 3 ClCN (gas) → $(ClCN)_3$ (liq.).

[‡] Although in acid medium thiocyanates isomerise readily into isothiocyanates[245], formation of the latter has not been observed in mixed cyclotrimerisation[243,244].

Table 6. Mixed cyclotrimerisation of cyano-compounds RCN and R'CN.

No.	R	R'	1,3,5-Triazines* (XLVII)	(XLVIII)	(XLIX)	(L)	Reactivity of cyano-compound: diene formation	dienophilicity	Ref.
1	Cl	H	+		(+)		RCN ≫ R'CN	R'CN > RCN	237
2	Cl_3C	CH_3; C_2H_5	+	–	–	–	RCN ≫ R'CN	R'CN ≫ RCN	40, 50, 238–240
3	Cl_3C	Alk	+	–	–	–	RCN ≫ R'CN	R'CN ≫ RCN	50**, 240
4	Cl_3C	RS	+	–	–	–	RCN ≫ R'CN	R'CN ≫ RCN	243***, 244
5	Cl_3C	Ar	+	–	–	–	RCN ≫ R'CN	R'CN ≫ RCN	40, 50, 241***, 242
6	Cl_3C	$C_2H_5O_2C$	+	+	+	+	RCN ~ R'CN	RCN ~ R'CN	40
7	Cl_2HC	CH_3	+	–	+	–	RCN ≫ R'CN	R'CN > RCN	243
8	$C_2H_5O_2C$; Cl	CH_3	+	–	+	–	RCN ≫ R'CN	R'CN > RCN	40
9	C_6H_5O	HO	+	(+)	–	–	RCN > R'CN	R'CN > RCN	246***
10	HS	Ar	+	–	–	–	RCN ≫ R'CN	R'CN ≫ RCN	246****

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*Symbols: + = trimer isolated; (+) = traces of trimer found; – = compound not formed.

**Mixed trimerisation proceeded better if the reaction mixture was heated to 150–200°C after the introduction of hydrogen chloride. In all other cases the reactions were conducted in the range from –40 to 25°C.

***Reaction conducted under pressure.

****Cyclotrimerisation took place in the absence of a catalyst.

Compound (XLVII) is formed only[67,238,239] when the molecular ratio RCN:R'CN $\leqslant$ 2.

The main product (XLVII) of the reaction between cyanogen chloride and hydrogen cyanide (2 : 1) is accompanied by traces of 2,4,6-trichloro-1,3,5-triazine (XLIX),[237] which indicates competitive addition of cyanogen chloride (RCN) to (LI). In the reaction between ethyl cyanoformate or cyanogen chloride and acetonitrile (2 : 1),[40] however, this last compound (R'CN) adds preferentially to (LI) (Table 6, No. 8).

If both cyano-compounds are able to form "dienes", three types of reaction are hypothetically possible. When the rates of formation of the "diene" (LI) and of subsequent addition of "its own" nitrile with separation of (XLIX) exceed the corresponding rates for the other nitrile, the homotrimerisation products (XLIX) and (L) should be formed exclusively. In the second alternative both "dienes" prefer to react solely with the "foreign" nitrile, and only the mixed trimerisation products (XLVII) and (XLVIII) should be formed. Neither type of reaction has yet been met in practice.

The third case—formation of all four structures (XLVII)-(L)—is realised with trichloroacetonitrile and ethyl cyanoformate (2 : 1) (Table 6, No. 6). The proportions on the products ($R = CCl_3$, $R' = C_2H_5COO$) can easily be controlled by varying the reaction conditions[40]. Thus initial treatment of trichloroacetonitrile with hydrogen chloride to form the "diene" followed by introduction of the ester yields (XLVII) as the main product. When hydrogen chloride is introduced into a mixture of the two nitriles, however, the main product will be (XLVIII): i.e. the rate of "diene" formation is greater from the ester than from the nitrile.[40]

Only qualitative information is available on uncatalysed mixed cyclotrimerisation[246]. The proportions of the products suggest[246] that RCN ≪ R'CN in "dienophilicity", while RCN ≫ R'CN in tendency to diene formation (Table 6, No. 9 and 10). A few cases of mixed cyclotrimerisation have been reported also in which nitriles are apparently formed as intermediate products during the reaction[67,240,241,247].

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In conclusion we must note the great theoretical and practical value of research on the cyclotrimerisation of compounds containing cyano-groups. As a consequence of the large number of investigations in this field, especially during recent years, the influence of the chemical structure of the initial cyano-compounds, the catalysts, and also several other factors has been elucidated. This in turn has permitted the directed synthesis of 1,3,5-triazines having valuable combinations of properties. For example, 1,3,5-triazines containing perfluorinated substituents are stable up to ~500°C and can be used as thermostable heat-transfer agents and lubricants.

Further fundamental research is required on the reaction mechanism. Mixed cyclotrimerisation of various cyano-containing compounds has great prospects, enabling the synthetic possibilities to be greatly extended.

At the present time several cyano-compounds—hydrocyanic acid, cyanogen chloride, cyanamide, acrylonitrile, etc.—are large-tonnage industrial products. Several 1,3,5-triazines (cyanuric chloride, melamine, cyanuric acid, and their derivatives) are produced on a large scale.

In view of the simplicity and technical importance of the cyclotrimerisation of compounds containing cyano-groups, industry may be expected in the near future to make use of many valuable new monomeric and polymeric products containing 1,3,5-triazine rings.

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Functional Group Analysis of Nitrogen- and Sulphur-containing Organic Compounds

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Data published during the last 7-9 years on problems concerning the determination of nitrogen- and sulphur-containing functional groups in organic compounds are surveyed.
The bibliography includes 281 references.

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II. Titrimetric methods for the determination of nitrogen- and sulphur-containing organic compounds 991
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I. INTRODUCTION

Methods of functional group analysis are of indepenent important both in industry, for the analysis of various industrial mixtures, and in the study of newly synthesised compounds. During recent years, three monographs have been published[1-3] on advances in analytical chemistry in the field of functional group analysis of organic compounds. However, they deal only with studies published up to 1967. This paper represents a review of studies on the analysis of various amines, amides, hydrazines, hydrazides, oximes, nitro- and nitroso-compounds, thiols, sulphides, disulphides, sulphonic acids, etc., carried out in 1968 to 1977.

Studies on analysis in recent years have been carried out with the following main aims: (1) the improvement of known analytical methods, their application to more complex systems, and detailed investigation of reaction mechanisms; (2) automation of methods involving the use of electrometric methods for the determination of the titration end point (amperometry, potentiometry, and coulometry); (3) the application of new chemical reagents; (4) the development of new analytical methods.

II. TITRIMETRIC METHODS FOR THE DETERMINATION OF NITROGEN- AND SULPHUR-CONTAINING ORGANIC COMPOUNDS

1. Acid–Base and Oxidation–Reduction Titration Methods

(a) Determination of amines. Acid–base titration is one of the classical methods for the analysis of nitrogen-containing organic compounds, but it has not been used on a sufficiently large scale until the non-aqueous titration technique became popular[4]. At present organic bases are widely determined by acid–base titration in research and in industry[5,6]. Comparatively recently a review has been published on methods for the determination of aromatic amines[7], which shows that the most general and easiest method for determining amino-groups is non-aqueous potentiometric titration. Thus a procedure has been proposed[8,9] for the non-aqueous potentiometric titration of polyethyleneamines and pyridyl-containing carbamates using a solution of $HClO_4$ in glacial acetic acid as the titrant. Solutions of neutral salts ($CaCl_2$, LiCl, NaCl, etc.) are sometimes used in the potentiometric determination of weak bases. The effectiveness of the above salts is determined by their influence on the hydrogen ion activity and entails an increase of the width and sharpness of the potential jumps. Kreshkov et al.[10] investigated certain features of potentiometric titration in solutions of alkali and alkaline earth metal chlorides and developed methods for the determination of amines; they also studied the influence of the salt solution on the pH shift. According to the authors[10], the best salts are LiCl and $CaCl_2$. Thus *m*-, *p*-, and *o*-phenylenediamines were titrated using $CaCl_2$ solutions; comparison of titration curves in a salt solution with the corresponding curves for the same substances in water shows that the use of a salt solution greatly improves the titration conditions. The error of the method is 0.3%.

Titration in a non-aqueous medium has been used for the joint determination of higher aliphatic amines and quaternary ammonium salts[11]. The method is as follows: the quaternary ammonium salt is converted into the perchlorate or iodide and the remaining amine is determined by titration with $HClO_4$. After the titration of the amine, mercury(II) acetate is added in order to convert the quaternary ammonium perchlorate or iodide into the highly basic quaternary ammonium acetate and the undissociated HgI_2:

$$2\,(R_4\overset{+}{N}\overline{I}) + Hg\,(CH_3COO)_2 \rightarrow 2\,(R_4\overset{+}{N}CH_3COO^-) + HgI_2 \quad .$$

HgI_2 is then dissolved in an excess of the mercury(II) acetate solution and the quaternary ammonium acetate is titrated with $HClO_4$:

$$R_4\overset{+}{N}CH_3COO^- + H^+ + ClO_4^- \rightarrow CH_3COOH + R_4\overset{+}{N}ClO_4^- \quad .$$

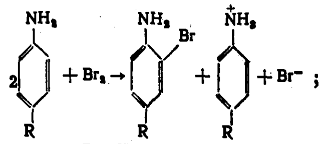
Since the basicity of all the compounds titrated is high, the final titration point is readily determined visually. For specimens with a ratio of tertiary amine to quaternary ammonium salt of 1 : 40, the results of the determination of the amine were reproducible to within 3–5% and those of the determination of the quaternary ion were reproducible to within 1–2%.

Potentiometric titration of a 0.1 *N* $HClO_4$ solution using differentiating non-aqueous solvents has been used to determine amine *N*-oxides. The methods for a quantitative determination of amine *N*-oxides are based mainly on their reduction to amines and the determination of the excess reductant. $SnCl_2$, $TiCl_3$, and HCl have been recommended as reductants[1]. However, these methods suffer from many limitations. Methods involving the direct titration of the *N*-oxides as bases are more promising[12].

Comparison of the ionisation constants of amines and *N*-oxides showed that aliphatic and saturated heterocyclic amines and their *N*-oxides with $pK = 4-5$ can be determined separately by potentiometric titration with $HClO_4$ in differentiating non-aqueous solvents. The interaction of amine *N*-oxides with protic acid solutions in dioxan, ethyl methyl ketone, and acetonitrile proceeds via a stage involving the formation of anomalous salts in which there are two molecules of the base per acid molecule. The method proposed[12] has been used to analyse mixtures of amine *N*-oxides and amides, hydrogenated aromatic heterocyclic bases, and the corresponding amines. Kwiatkowski et al.[13] used potentiometric titration in dimethyl sulphoxide (DMSO) with the aid of glass electrodes to analyse di-(n-butyl)amine, tri-(n-butyl)amine, piperidine, *N*-ethylpiperidine, allylamine, isobutylamine, diethanolamine, etc.

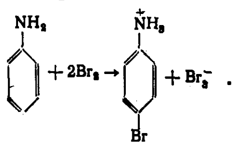
Careful studies of potentiometric titration in non-aqueous media are being continued and the influence of the titrant concentration, temperature, and amine structure is being investigated. Apart from $HClO_4$, the titrants used in the determination of amines are HCl, H_2SO_4, and toluene-*p*-sulphonic acid, dissolved in DMSO.[13] However, in many instances, particularly in the analysis of the products of synthesis, precipitates or tarry substances are formed during the titration, coat the electrodes, and interfere with a clear-cut determination of the titration end point. The high-frequency titration method, which is free from this disadvantage, was therefore used in the determination of certain aromatic amines[15]. This procedure has been used successfully for the overall and separate determination of primary and secondary amino-groups in polyethylenepolyamines and products of synthesis based on them. A TV-61 high-frequency titrator was employed; the determinations were carried out mainly by the back-titration method, since the equivalence point is then determined more clearly. A suitable solvent, ensuring the most distinct inflections in the titration curve, was selected for each compound.

The bromination method is frequently used for the quantitative determination of amines. The bromide–bromate system, which evolves bromine in an acid medium, has come to be employed as a source of bromine. However, this method requires the use of aqueous solutions which has limited its applications to the determination of amines. In recent years a number of studies have been made on titration with bromine in non-aqueous solutions[16-19]. Krause and Kratochvil[16] determined a number of aromatic amines to within 1% using propylene carbonate as the solvent. Propylene carbonate is a convenient medium for the bromination of amines, is resistant to the action of the halogen, has a high dielectric constant which increases the rate of reaction, is soluble in water, colourless, and non-toxic. The majority of amines are soluble in propylene carbonate. In many cases the bromination takes place in the presence of bases such as pyridine (in order to bind the evolved protons). Like the hydroxy-group, the amino-group activates the *ortho*- and *para*-positions in electrophilic aromatic substitution. Since primary amines are proton acceptors, the bromination of certain amines in propylene carbonate is possible without the addition of a base. In the titration of *p*-phenetidine, *p*-toluidine, and aniline the potential increases sharply when 1-2 equivalents of bromine has been added. This can be explained by the reaction

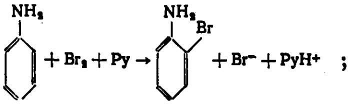


$R = CH_3$, H, or OC_2H_5.

Since the monobrominated aromatic amine is a weaker base than the non-brominated amine, the protons produced in the substitution stage apparently combine with the non-brominated amine. The protonated amine is not brominated subsequently, since the protonated amino-group hinders electrophilic substitution. The second potential jump in the absence of pyridine occurs after the addition of two moles of bromine per mole of aniline:

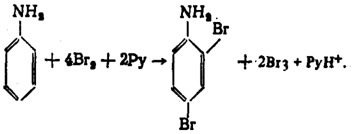


When pyridine is present in the reaction mixture, two potential jumps also occur. The first takes place after the addition of one equivalent of bromine:



Py- pyridine.

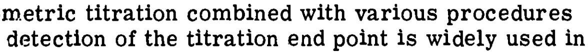
The second occurs after the addition of four moles of bromine per mole of aniline:



p-Toluidine behaves similarly to aniline. The introduction of a third bromine atom in the free *ortho*-position of aniline is apparently difficult, although after the addition of six moles of bromine a very small potential jump does appear[16].

Analysis of *m*-phenylenediamine by titration with bromine is possible both in the presence of pyridine and in its absence. The bromide–perbromide system in pyridine[17] (PBPB, $C_5H_5N.HBr.Br_2$), each molecule of which readily evolves one molecule of free bromine, may be used as the source of bromine. The greater availability of crystalline PBPB compared with the bromide–bromate solution and high reaction rates with minimal side reactions make this method more suitable in both preparative and analytical chemistry. The above system had been used previously to brominate substituted phenols and aromatic amines and aliphatic and alicyclic ketones in acetic acid[18]. The system has been used[17] to determine aniline and various monosubstituted anilines. The majority of reactions were rapid (over a period of 10–15 min); the concentration of the amine analysed was 10^{-4} M and the error of the method was $<1\%$. The end point was determined spectrophotometrically; photometric titration is possible only for colourless or slightly coloured products, which is a significant disadvantage of this method.

Sotsenko et al.[19] modified the bromide–bromate method for the determination of aromatic amines in various solutions. The essential feature of their procedure reduces to analysis in a specially designed diffusion apparatus with addition of a known excess of a standard bromide–bromate solution. In an acid medium the free bromine evolved brominates, for example, aniline to tribromoaniline and its excess is absorbed by a potassium iodide solution deposited on a porous material (filter paper or synthetic water-soluble paper). The titration of the iodine, evolved in an amount equivalent to that of the absorbed bromine, is carried out in the same apparatus with sodium thiosulphate solution; the time required for the analysis is 10 min at 40°C or 17 min at room temperature, and the accuracy of the determination is to within 1.5%. This method can be used to analyse dark or intensely coloured solutions. Sotsenko et al.[19] analysed *m*-toluidine, anthranilic acid, sulphanilic acid, and anilinium chloride. In the determination of semicarbazide hydrochlorides Campbell et al.[20] used successfully titration with potassium bromate in the presence of metal ions (nickel, cobalt, and manganese). Semicarbazides are determined with $KBrO_3$ in accordance with the following scheme:

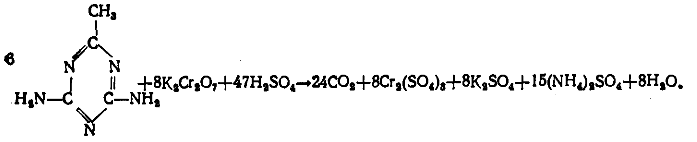


$$3NH_2\underset{\overset{\|}{O}}{C}NHNH_2 + 2BrO_3^- \rightarrow 2N_2 + 3CO_2 + 3NH_3 + 2Br^- + 3H_2O \quad .$$

Iodometric titration combined with various procedures for the detection of the titration end point is widely used in the determination of organic compounds. A thermometric titration method, in which alicyclic and aliphatic amines and hydrazines are titrated with iodine in non-aqueous solutions containing alkyl vinyl ethers, which polymerise exothermically in the presence of an excess of iodine, has been described[21]; the titration end point is determined on the basis of the exothermic polymerisation reaction. This method has an accuracy to within 1% in most cases.

In the above study iodine was used both as the titrant and as the catalyst of the cationic polymerisation and ethyl vinyl ether was employed as the monomer. Among organic bases, aliphatic and alicyclic amines have been determined by this procedure, namely n-butylamine (3.6), benzylamine (3.7), piperidine (3.6), tris(hydroxymethyl)-methylamine (4.3), 2-*N*,*N*′-diethylaminopropionitrile (4.4), *N*-methylmorpholine (4.6), etc.; pyridine derivatives, namely pyridine (4.1), *α*-picoline (3.8), pyridine-2,6-dicarboxylic acid (0.09), pyridine *N*-oxide (2.2), 3-picoline *N*-oxide (2.2), etc.; aniline derivatives, namely aniline (1.3), *o*-toluidine (1.5), diphenylamine (0), triphenylamine (0), etc.; and heterocyclic nitrogen-containing compounds, namely hexamethylenetetramine (5.0), phthalazine (3.5), quinoline (0), and benzimidazole (4.0). The number of iodine atoms consumed per molecule of the test compound is indicated in brackets. It is believed[21] that the number of iodine atoms reacting with the molecule of the base may be used as a measure of the strength of the base.

The titrimetric method involving oxidation by $K_2Cr_2O_7$ has been used successfully[22] to determine acetoguanamine in the presence of melamine and guanidine; the excess oxidant was determined iodometrically:



$$+8K_2Cr_2O_7+47H_2SO_4\rightarrow 24CO_2+8Cr_2(SO_4)_3+8K_2SO_4+15(NH_4)_2SO_4+8H_2O.$$

A method of direct potentiometric titration of various amines by hypobromite, based on the hydrogen substitution reaction in the amino-group has been proposed[23]:

$$RNH_2 + 2BrO^- \rightarrow R{-}NBr_2 + 2OH^- \quad ,$$
$$R_2NH + BrO^- \rightarrow R_2{-}NBr + OH^- \quad .$$

The authors[23] tested the method on 40 different compounds.

(b) Determination of hyrazine and its derivatives. A monograph[24], which describes a comparative analysis of all the existing methods and examines in detail the reaction mechanisms and the influence of various factors on analytical results, is devoted to various methods for the determination of hydrazine and its derivatives. Malone[25] proposed an acid–base isocyanate method for the determination of mixtures of hydrazine with 1,1-dimethylhydrazine and monomethylhydrazine. The method is based on the difference between the rates of reaction of isocyanate with the corresponding hydrazines in anhydrous acetic acid solution; the rate of reaction decreases in the sequence hydrazine > monosubstituted hydrazine ≫ disubstituted hydrazine. An alcoholic HCl solution was used as the titrant, the accuracy of the method being to within 0.1 to 0.5%. A method involving direct non-aqueous titration in dimethylformamide (DMF) by strong bases has been proposed for the determination of *N*,*N*′-diacylhydrazines[26]. Tetrabutylammonium hydroxide or potassium t-butoxide were proposed as titrants in the presence of 2-nitroaniline as the indicator.

Titration with a solution of ICl in 5 *N* HCl has been used recently[27] to determine hydrazine, phenylhydrazine, *p*-nitrobenzoic hydrazide, semicarbazide, and isonicotinic acid hydrazide; the oxidation is in all cases rapid and quantitative. Amperometric titration methods for the determination of certain mono- and di-substituted hydrazines with a permanganate solution at pH 6–7 have been described[28]. The relative standard error in ten replicate experiments was 3%. Subsequently the method was improved[29], using as the medium an aqueous acetone solution in which the potentials of the onset of the oxidation of hydrazine and dimethyl hydrazine at a platinum anode differ sharply. The reaction mechanism is based on the difference between the rates of oxidation by potassium permanganate of the products of the interaction of hydrazine and dimethylhydrazine with acetone in the presence of $Na_4P_2O_7$. A solution of potassium dichromate may be used as the oxidant; the accuracy of the method is to within 0.5%.[30]

(c) Determination of amides and nitriles. A review has been devoted to the determination of amides and nitriles[31]; the authors discuss the principal methods for the determination of amides: hydrolysis (alkaline, acid, and catalytic), potentiometric and amperometric titration, reduction with $LiAlH_4$, and colorimetry. For nitriles, there are as yet no specific analytical methods, which makes it very difficult to determine them chemically in mixtures with nitrogen-containing compounds. Hydrolysis yields satisfactory results only for primary aliphatic nitriles. Reports have been published recently about new methods for the determination of organic compounds of this class, which are discussed in detail in Section IV.

(d) Determination of oximes and their derivatives. The principal methods for the determination of compounds of this class are given in a monograph[1]. The latest studies[32,33] were devoted to potentiometric non-aqueous titration of mono- and di-oximes and benzohydroxamic acids with a 0.1 *N* solution of tetrabutylammonium hydroxide. In all cases a clear-cut end point, corresponding to one mole of base for one mole of oxime, was obtained. The influence of the solvent on the change in potential at the end point has been discussed[32,33]. An attempt[34] to modify the iodometric method for the determination of hydroxylamines (Blom's method) was unsuccessful; the authors studied the oxidation reaction in detail and proposed a mechanism:

$$\begin{gathered}RCH_2NHOH \xrightarrow{I_2} RCH{=}NOH \quad ,\\ RCH{=}N{-}OH \overset{H_2O}{\rightleftarrows} RCHO + NH_2OH,\\ NH_2OH \xrightarrow{I_2} NO_2^- \quad .\end{gathered}$$

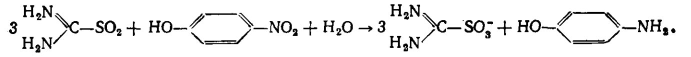
The amount of nitrite formed from hydroxylamine derivatives depends on the rate of hydrolysis of the intermediate oxime; if the latter is low, the quantitative determination of nitrite is difficult. For this reason, the method is used only for qualitative analysis.

(e) Determination of nitro-compounds, nitroso-compounds, and nitrosamines. Aromatic nitro- and nitroso-compounds are determined by reduction either with Fe^{2+} in an acid or alkaline medium[35,36] or with an excess of titanium chloride solution[37]. An interesting method, involving the aquametric determination of nitro-compounds, based on their reduction by $SnCl_2$ in anhydrous acetic acid to the amine and water and subsequent determination of the evolved water with Fischer's reagent, has been proposed[38]:

$$RNO_2 + 3SnCl_2 + 6HCl \rightarrow RNH_2 + 3SnCl_4 + 2H_2O \quad .$$

The excess $SnCl_2$ was titrated with an anhydrous solution of iodine in DMF. Thus the content of NO_2 groups was estimated simultaneously by both potentiometric and aquametric methods. The titration end point was in both cases established biamperometrically using the $I_2 \rightleftharpoons 2I^-$ system; the accuracy of the method is to within 0.5%.

It has been suggested that thiourea dioxide (TUD) be used for the determination of nitro-groups in phenols[39]. The essential feature of the method consists in the quantitative reduction of the nitro-groups to amino-groups:



The aminophenols formed were determined spectrophotometrically.

Methods for the determination of nitrosamines are described in detail in reviews[41,42], where the chemical properties, biological activities, and methods of analysis of compounds of this class are considered. A sensitive method for the determination of nitrosamines consists in their reduction by $LiAlH_4$ to hydrazine and condensation of the latter with anthracene-9-aldehyde or phenanthrene-9-aldehyde, which leads to the formation of highly fluorescent hydrazones. After their isolation, the hydrazones are identified spectrophotometrically or mass-spectrometrically[43]. Mention should also be made of a new interesting reagent used to determine various functional nitrogen-containing groups, namely 1-chloro-3-ethylpent-1-en-4-yn-3-ol (Placidyl)[44]. This reagent can be used in various solvents (C_2H_5OH, $CHCl_3$, CCl_3CCl_3) to test for ureas, primary aromatic amines, *sym*-alkylhydrazines, and indole derivatives.

(f) Determination of thiols. One of the most frequently used methods for the determination of thiols is oxidative titrimetry. Direct and back titration with iodine, accompanied by the visual or potentiometric indication of the end point, are used[45-48]. The mechanism of the oxidation of thiols to disulphides has been studied in detail comparatively recently[48] and may be represented schematically as follows:

$$\begin{array}{l}2RSH + 2H_2O \rightleftarrows RSSR + 2\overset{+}{H_3}O + 2e^- \quad ,\\ 2e^- + (I_2)_{aq} \rightleftarrows 2I^- \quad ,\\ \hline 2RSH + (I_2)_{aq} + 2H_2O \rightleftarrows RSSR + 2I^- + 2H_3O^+ \quad .\end{array}$$

In an anhydrous medium the reaction does not go to completion owing to the reverse protolytic reaction

$$2H_3^+O + 2I^- \rightleftarrows 2HI + 2H_2O \quad .$$

The reducing effect of HI predominates. The reaction involving t-butylmercaptan proceeds to the sulphenyl iodide:

$$R_3CSH + I_2 \rightleftarrows R_3CSI + HI \quad .$$

The side reaction

$$R_3CSI + RSH \rightleftarrows R_3CSSR + HI$$

is suppressed with lead(II) nitrate, which forms the mercaptide and then lead iodide:

$$(RS)_2Pb + I_2 \rightleftarrows RSSR + PbI_2 \quad .$$

It has been shown[48] that there is a tendency towards further oxidation to higher oxidation states of sulphur, so that errors in the determination of certain thiols are possible.

Together with iodine, bromine or a bromide–bromate solution are used[49-51]. They are stronger oxidants than iodine and increase the degree of oxidation of the disulphide. The titration with bromide–bromate, proposed previously for the determination of sulphides and disulphides in acetic acid, has been used to determine thiols with potentiometric indication of the end point using platinum or graphite electrodes[49]. The potential jump corresponds to the reaction

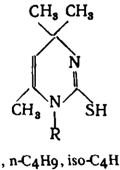
$$RSH + 3Br_2 + 7H_2O \rightleftarrows RSO_2Br + 5H_3\overset{+}{O} + 5Br^- \quad .$$

Aromatic thiols are oxidised quantitatively to sulphonyl bromides, while the reaction involving aliphatic thiols proceeds with difficulty. The sensitivity of the method is to within 5×10^{-8} M thiol. Apart from the bromide–bromate system, a study was made of the $Pb(CH_3COO)_4/Pb(CH_3COO)_2$ system[49], which has a still higher standard oxidation potential, but the oxidation of thiols to the sulphonic acids in anhydrous acetic acid was not observed. This is probably caused by the solvolysis in this medium. Only the following reaction takes place:

$$2RSH + (CH_3COO)_4Pb \rightleftarrows RSSR + (CH_3COO)_2Pb + 2CH_3COOH \quad .$$

The reaction is used in both potentiometric and visual titration with an indicator to determine primary aliphatic thiols with a long chain and aromatic and heterocyclic thiols[51].

Potassium or sodium periodate in dilute sulphuric acid has been used for the quantitative determination of primary and secondary thiols[52]. Thiocarbonyl compounds and sulphocyanamide ions interfere with the determination. The same method has been used[53] to determine 2-mercaptopyrimidines of the type



R = H, CH_3, n-C_4H_9, iso-C_4H_9, C_6H_5, 3-$NO_2C_6H_4$, or 2-NO_2-4-$CH_3C_6H_3$.

One of the oldest methods for the determination of thiols involves their oxidation with copper(II) salts. Nowadays the reaction is usually carried out in DMF with potentiometric indication of the end points, using platinum, graphite, or copper electrodes[54]. The oxidation of thiols by potassium hexacyanoferrate(III) $K_3[Fe(CN)_6]$ proceeds quantitatively only in an alkaline medium[54,55], but, since the oxidation of thiols is accelerated in air under these conditions, the determination must be carried out in an inert gas atmosphere; in the back titration ascorbic acid must be used to determine the excess $[Fe(CN)_6]^{3-}$. The accuracy of the method is to within 1.5%.

Iodine chloride and bromide and iodine and bromine cyanides are used very frequently to determine thiols[56-58]. The method is based on the oxidation of thiols to disulphides:

$$2RSH + IX \rightleftarrows RSSR + HI + HX;$$
$$X = Cl,\ Br,\ or\ CN.$$

The reaction is carried out in an aqueous or anhydrous medium with potentiometric or visual indication of the equivalence point. The somewhat unstable results obtained when iodine cyanide is used[57] are associated with the formation of hydrogen iodide, which is a powerful oxidant. Its influence can be eliminated by adding benzene, because HI is soluble in water and thiols are soluble in benzene. Bromine cyanide is more convenient than iodine cyanide, because HBr is a weaker reductant. The accuracy of the method is to within 0.25%. Thiocarbonyl compounds, sulphides, and thiocyanate ions interfere with the determination. It has been found recently[59] that, in the presence of acetic acid, thiols are readily and quantitatively oxidised to disulphides by *N*-bromosuccinimide. However, this method is inconvenient owing to the low solubility of *N*-bromosuccinimide in water and the changes in its solutions with time.

A number of methods for the determination of thiols are based on the formation of insoluble or undissociated mercaptides. These are primarily reactions with silver and mercury ions. Silver salts had been frequently used previously to determine thiols by amperometric titration[2], but, in view of the difficulty of determining the end point, potentiometric determinations have come to be used. During recent years, methods have been developed for the determination of thiols using silver electrodes[60-64] with solutions of mercury salts and silver nitrate as titrants. Apart from mercury salts, organomercury compounds, which are more selective for the thiol group, are frequently employed. *p*-Dimethylaminophenylmercury acetate and *p*-diethylaminophenylmercury acetate[65,66] have been proposed for the visual, potentiometric, and amperometric titration of thiols (the error of the method is $<1.5\%$).

Qualitative tests for the mercapto-group must also be mentioned. Thus the reaction of thiols with 2,2-dithiobis-(5-nitropyridine) leads to the appearance of a yellow colour due to the formation of 5-nitropyridine-2-thione[67]. This reaction is used for the detection of thiols in paper and thin-layer chromatography. Another sensitive test for the SH group is reaction with $Hg(CN)_2$,[68] which leads to the formation of mercury mercaptide and HCN. The evolution of the latter may be detected from the appearance of a blue colour in filter paper impregnated with a solution of tetrabase or copper ethylacetoacetate in chloroform. The minimum amount of thiols which may be determined is 1–5 μg.

(g) Determination of sulphides and disulphides. The principal methods for the determination of sulphides and disulphides have been described fairly completely in a monograph[1] and in conference proceedings[3,6]; during recent years, few studies have been published on the analysis of compounds of this class. Thus a method involving acid–base potentiometric titration with sodium hydroxide in DMF has been proposed for the analysis of bis-(2-carboxyphenyl) disulphide[69]. Potentiometric titration (using a silver sulphide electrode) by silver salts has been employed for the separate determination of thiols and disulphides in a mixture[48]. The thiol is titrated initially and then sodium sulphite is added, the latter reacting with the disulphide as follows:

$$RSSR + SO_3^{2-} \rightarrow RS^- + RSSO_3^- \quad .$$

The mercaptan produced is titrated with silver salts. The disulphide group is frequently reduced to the mercapto-group and all the analytical methods for the determination of thiols can be used. Many reagents have been proposed for the reduction of disulphides[64,70,73], but none of them are universal. Best results have been obtained for the solution $LiAlH_4$ in tetrahydrofuran (THF).

Wronski[64] proposed a new reagent—sodium aluminium bis-(2-methoxyethoxide) dihydride (70% solution in benzene):

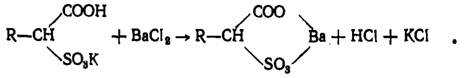
$$NaAlH_2(OCH_2CH_2OCH_3) + RSSR \rightarrow NaAl(SR)_2(OCH_2CH_2OCH_3) + H_2 \quad .$$

Decomposition with water yields thiols, hydrogen sulphide, sodium hydroxide, aluminium hydroxide, and α-methoxyethanol. The method is applicable to aliphatic and aromatic disulphides and its accuracy is to within 5%. Sulphides and disulphides are usually determined by methods based on their oxidation with periodate to the corresponding sulphoxides[71]. A solution of phenyliodoso acetate in dilute acetic acid has been proposed as the oxidant[72]:

$$RSSR + 4PhI(OCOCH_3)_2 + 4H_2O \rightarrow RSO_2SO_2R + 4PhI + 8CH_3COOH \quad .$$

The excess of phenyliodoso acetate is reduced with ascorbic acid and titrated with a solution of iodine. The method can be used also for the analysis of a mixture of thiols, sulphides, and disulphides; it is accurate, rapid, and does not require special conditions.

(h) Determination of sulphonic acids, sulphinic acids, thioureas, and dithiocarbamates. The principal method for the analysis of sulphonic acids is alkalimetry. In recent years many technological products have been analysed by this procedure, and mixtures of isomeric sulphonic acids have been determined. Thus an attempt has been made[74] at the separate determination of toluene-*o*- and toluene-*p*-sulphonic acids by high-frequency titration in non-aqueous media. Kreshkov and coworkers[75] developed a differential titration method (with the aid of KOH) for the determination of a mixture of aminobenzenesulphonic acids, the accuracy of the method being to within 2–6%. Certain substituted aromatic sulphonic acids are determined by potentiometric titration with sodium methoxide in pyridine or acetone[76], but the accuracy is low. In the determination of a mixture of isomeric sulphonic acids the latter are frequently subjected to preliminary separation on a column with cation-exchange resins[77]; the accuracy of the method is to within 1%. A specific method[78] for the determination of α-sulphocarboxylic acids is based on their ability to cyclise readily to form a six-membered ring with alkaline earth metal ions, particularly the barium ion:



$$R{-}CH(COOH)(SO_3K) + BaCl_2 \rightarrow R{-}CH(COO)(SO_3)Ba + HCl + KCl \quad .$$

Thus the determination of α-sulphocarboxylic acids can be reduced to the determination of hydrochloric acid. The titration is carried out in a 1 : 1 water–isopropyl alcohol medium with strong bases.

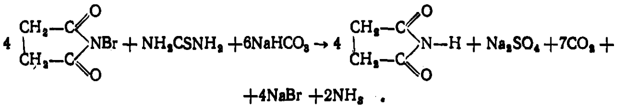
Iodometric titration has been used to determine sodium noramidopyrinemethanesulphonate[79].

A method for the quantitative determination of sulphinic acids[80,81] is based on the reaction with nitrous acid:

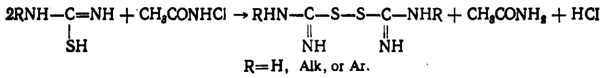
$$2RSO_2H + HONO \rightarrow (RSO_2)_2NOH + H_2O \quad .$$

The reaction is carried out in a strongly acid medium, the end point being determined potentiometrically or amperometrically; the accuracy is to within 0.8%.

Thiourea and its derivatives are readily determined by oxidative titrimetry. A method for the determination of thiourea by its direct titration with $KMnO_4$ in sulphuric acid has been described[82]; the end point is distinct and stable. Thiourea can be oxidised quantitatively to the sulphate with potassium dichromate in sulphuric acid[83]. The excess dichromate is titrated with ferrous ammonium sulphate; it is noteworthy that, under these conditions, thiocyanates are also oxidised; the accuracy of the method is to within 0.5%. It was shown subsequently that[84] the presence of copper(II) ions greatly accelerates the reaction. It has been suggested recently that *N*-bromosuccinimide be used as an oxidant for thiourea[85,86] (the reaction is carried out in the presence of sodium bicarbonate):



N-Chloroacetamide has also been proposed as a thiourea oxidant[87] (for potentiometric and visual titration):

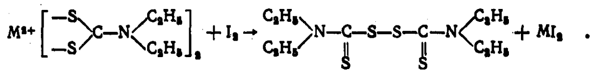


$$2RNH{-}\underset{\displaystyle SH}{\underset{|}{C}}{=}NH + CH_3CONHCl \rightarrow RHN{-}\underset{\displaystyle NH}{\underset{\|}{C}}{-}S{-}S{-}\underset{\displaystyle NH}{\underset{\|}{C}}{-}NHR + CH_3CONH_2 + HCl$$

$$R{=}H,\ \text{Alk, or Ar.}$$

Potassium iodate is used successfully to oxidise thiourea to the disulphate[70,88]. One of the old methods for the oxidation of thiourea consists in its titration by silver salts in an ammoniacal medium in the presence of dithizon[89]. This procedure is also used for the joint determination of thiourea and thiocyanates[90]. The ability of thiourea to form stable insoluble compounds with silver ions has been used to make silver halide membrane electrodes, which are employed for the potentiometric determination of thiourea[91,92].

In view of the great practical importance of dithiocarbamates (as fungicides), a review was published comparatively recently by Halls[93], which the principal method for the determination of compounds of this class are analysed. The majority of the methods are based on the decomposition of dithiocarbamates in an acid medium and the determination of carbon disulphide. Oxidative methods of determination are also discussed. The determination of water-insoluble bivalent mercury, lead, cadmium, and zinc ions as the diethyldithiocarbamates by titration with a solution of iodine and chloroform has been proposed[94]:



$$M^{2+}\left[\begin{matrix}{-}S\\{-}S\end{matrix}\!>\!C{-}N\!<\!\begin{matrix}C_2H_5\\C_2H_5\end{matrix}\right]_2 + I_2 \rightarrow \begin{matrix}C_2H_5\\C_2H_5\end{matrix}\!>\!N{-}\underset{\displaystyle S}{\underset{\|}{C}}{-}S{-}S{-}\underset{\displaystyle S}{\underset{\|}{C}}{-}N\!<\!\begin{matrix}C_2H_5\\C_2H_5\end{matrix} + MI_2 \quad .$$

The end point is determined visually or spectrophotometrically. Iodine chloride[95] and iodine and bromine cyanides[96] are also used as oxidants for dithiocarbamates; the accuracy of the method is to within 0.5%. The influence of the pH of the medium, the nature of the solvent, and the nature of extraneous ions has been investigated[95]. Methods have been proposed for the determination of dithiocarbamates with the aid of the iodine–azide reaction[97] and potentiometric titration with perchloric acid in an anhydrous medium[98]. A method involving the direct titration of dialkyl and diaryl phosphorodithioites with dimethyl- and diethyl-aminophenylmercury acetates has been developed[99]. Mention should be made of studies[5,100] in which a method has been proposed for the coulometric analysis of a technical mixture of sulphenamides and dibenzothiazolyl sulphide, based on the oxidation of solutions in acetic acid with bromine. The separate determination of the mixture components is based on their different solubilities in the organic solvent.

2. Titration with Preliminary Chemical Reactions

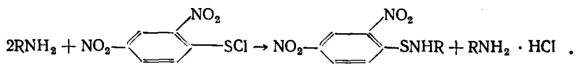
a. Determination of nitrogen-containing organic compounds. A widely used method for the determination of tertiary amines in the presence of secondary and primary amines is titration in glacial acetic acid with a solution of perchloric acid after preliminary acylation with acetic anhydride[101]. However, quantitative acylation of certain amines by acetic anhydride requires severe conditions. It has been suggested[102] that trifluoroacetic anhydride be used as the acylating agent. The acylation reaction proceeds at room temperature; the error is 0.4%. Isopropenyl acetate can be used successfully as the acylating agent[103], its acylating capacity being superior to that of keten and acetic anhydride; the compound is of interest for the acylation of readily enolised compounds; the accuracy of the method is to within 0.1–0.4%. The formaldehyde–sodium bisulphide complex reagent is frequently used in the iodometric determination of amines[104-106]; it reacts with the amino-group to form methanesulphonates, which are titrated with a solution of iodine in an aqueous acid medium. Aniline and its derivatives[104], toluidines, and xylidenes[105] have been determined by this method; its accuracy is to within 0.5%.

The cyanoethylation reaction has been used for the determination of primary and secondary amines[107]; the amines react with acrylonitrile in accordance with the equations

$$RNH_2 + CH_2{=}CHCN \rightarrow RNHCH_2CH_2CN \, ,$$
$$R_2NH + CH_2{=}CHCN \rightarrow R_2NCH_2CH_2CN \, .$$

The reaction is accelerated by catalysts (water and acids) and takes place at room temperature for the majority of amines. The excess acrylonitrile is titrated by the sulphite method.

Obtemperanskaya and Kalinina[108] suggested that 2,4-dinitrobenzenesulphenyl chloride be used for the determination of aliphatic and aromatic amines; it reacts over a period of 10–15 min with the amine in benzene solution, forming 50% of the amide and 50% of the amine hydrochloride:



The employment of pyridine greatly accelerates the reaction and improves the yield of the product. The determining factor in the reaction is the change in the pK_b of the amine; one should note that amines with $pK_b \geq 11$ do not react (diphenylamine); the error is <1%. Since the reagent is highly hygroscopic, the authors subsequently replaced it by 2-nitrobenzenesulphenyl thiocyanate[109]. The method[109] is based on the reaction of these compounds in the presence of a small amount of alkali:

$$RNH_2 + NO_2C_6H_4SSCN \xrightarrow{NaOH} NO_2C_6H_4SNHR + NaSCN + H_2O \quad .$$

The excess reagent is decomposed with an aqueous solution of alkali. The sulphenamide formed reacts with hydrochloric acid to form sulphenyl chloride, which interacts quantitatively with potassium iodide to form iodine:

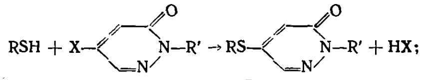
$$NO_2C_6H_4SNHR + 2HCl \rightarrow NO_2C_6H_4SCl + RNH_2 \cdot HCl \quad ,$$
$$2NO_2C_6H_4SCl + 2KI \rightarrow (NO_2C_6H_4S)_2 + I_2 + 2KCl \quad .$$

The liberated iodine is titrated with sodium thiosulphate; the accuracy of the method is to within approximately 1%. The application of these reagents in analytical chemistry has many advantages over methods based on the acylation reaction and acid–base titration.

Primary and secondary amines may be determined quantitatively by reaction with 1-(isothiocyanatomethyl)-isatin, in which crystalline urea derivatives are formed readily[110]. Phenyl isocyanate has been suggested[111] for the determination of primary and secondary amines. The thiourea derivatives formed are titrated with potassium iodate in an acid medium at room temperature.

Among the titrimetric methods for the determination of amino-compounds used at the present time, mention should be made of titration with bivalent metal (Cu^{II} and Mn^{II}) salts. For example, α-amino-acids have been determined[112] by titration with a solution of copper(II) sulphate, the maximum error being 0.3%. Aminopolycarboxylic acids are analysed by titration with Mn^{2+} salts[113-115]. A solution of N-chlorosuccinimide in the presence of Methyl Red as the indicator has been suggested for the determination of microamounts of hydrazines and their salts[116]. The end point is determined from the disappearance of the colour of the indicator. A 0.1 N solution of N-chloroacetamide has been used for the potentiometric analysis of hydrazine derivatives[117], the error of the method being ±0.8%. Potentiometric oxidative titration of oximes is carried out with $K_7Cu(HTeO_6)_2$.[118] The reagent is prepared by oxidising copper(II) to copper(III) with $K_2S_2O_8$ in KOH solution in the presence of $K_2Te_2O_7$ as the complex-forming agent.

b. Determination of organic sulphur compounds. Many methods for the determination of thiols involving phenylation by various reagents have been proposed. It has been suggested that 3-phenothiazinone in 80% acetic acid be used for the back titration of thiols[119]; the excess is titrated with sodium thiosulphate. The same reagent is suitable for the determination of thiourea and thiosemicarbazides. The titration of thiols with 4,5-dibromo-6-pyridazinone or 4,5-dichloro-6-pyridazinone in aqueous or organic media takes place quantitatively with elimination of an equivalent amount of the hydrogen halide[120]:



X = Cl or Br.

Side reactions with other nucleophiles, amines, phenols, sulphides, and alcohols were not observed. In a series of studies for the determination of thiols[121-126] new reagents have been proposed and analytical methods devised. We believe that vinyl sulphones are interesting reagents[112]. Owing to the presence of the electron-accepting sulpho-group, they readily react with nucleophiles via the terminal carbon atom attached to the double bond:

$$R{-}SO_2{-}CH{=}CH_2 + R'SH \rightarrow RSO_2CH_2CH_2SR' \quad .$$

A three-fold excess of a solution of the vinyl sulphone in dioxan is added to the thiol being analysed, the excess being titrated by the sulphite method. Aliphatic, aromatic, and heterocyclic mercaptans may be determined by this procedure. A method, which had been used earlier for the analysis of aliphatic and aromatic mercaptans and is based on nucleophilic addition to acrylonitrile, has been suggested for the quantitative determination of heterocyclic thiols[121]; the accuracy is to within 0.5%.

Arenesulphenyl halides are highly reactive in relation to thiols[123-126]; the reaction results in the formation of asymmetric disulphides:

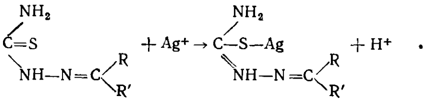
$$RSH + ClSC_6H_3(NO_2)_2 \rightarrow RSSC_6H_3(NO_2)_2 + HCl \quad .$$

It is carried out in acetic acid, the excess reagent being determined iodometrically. Aliphatic and aromatic thiols containing OH, NH_2, and COOH groups can be determined by this method In the reaction with heterocyclic thiols it is necessary to add pyridine in order to bind the hydrogen chloride. The error of the method does not exceed 1%. In the potentiometric titration of thiols with tetraethylammonium hydroxide, it is necessary to add 1-chloro-2,4-dinitrobenzene, which leads to a sharp increase of the potential jump[125].

Chloramine-T has been suggested as the oxidant for the analysis of thiosemicarbazides[127]; the reaction takes place quantitatively under the usual conditions:

$$NH_2NHCSNH_2 + 6\,[CH_3C_6H_4NCl]^- + 6H_2O \rightarrow 6CH_3C_6H_4SO_2NH_2 +$$
$$+ 6Cl^- + CO_2 + N_2 + \overset{+}{N}H_4 + H^+ + SO_4^{2-} \quad .$$

The excess chloramine-T is determined iodometrically. Thiocyanates and hydrazines interfere with the determination of thiosemicarbazides. Despite the enormous importance of thiosemicarbazones in pharmacology, until recently there were no suitable methods for their quantitative determination. Comparatively recently Campbell et al.[128] proposed a simple and rapid method for the quantitative determination of aromatic monothiosemicarbazones by the potentiometric titration of the protons liberated on formation of the complex with silver ions:



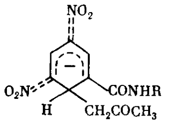
The accuracy of the method is to within 0.5%, but the procedure cannot be extended to all types of thiosemicarbazones and requires further development. The same workers[129] used copper(II) instead of silver for the determination of alkylbisthiosemicarbazones by an analogous procedure, the accuracy of which is to within 0.5%.

III. PHOTOMETRIC METHODS FOR THE DETERMINATION OF NITROGEN- AND SULPHUR-CONTAINING ORGANIC COMPOUNDS

A method widely used in recent years for the determination of nitrogen-containing organic compounds has been photometric analysis [3,24]. A number of investigators have developed new procedures for the determination of amines, amides, hydrazines, oximes, azo-compounds, etc. by colorimetric methods using various chemical reagents, which can be nitro-compounds, aromatic halogeno-derivatives, dyes, metal ions, etc. Most of these are readily available, and the analytical methods are simple and highly sensitive. There have been few studies in recent years on the photometric analysis of sulphur-containing organic compounds.

1. Photometric Analysis Using Organic Reagents

a. Determinations with nitro-compounds. Various aromatic nitro- and polynitro-derivatives, which give rise to intensely coloured solutions in acetone in the presence of strong alkalis, are fairly frequently used for the quantitative determination of nitrogen-containing compounds. The procedure is based on the Janowsky reaction, in which acetone interacts with the dinitro-compound in the enolic form, forming a quinonoid structure of the following type:



Comparatively recently Malone [130] investigated the interaction of hydrazine and amine derivatives with 20 different nitro-compounds and established that all the nitro-compounds which he proposed are suitable under certain conditions for the quantitative analysis of nitrogen-containing compounds. Bartos showed [131,132] that nitromethane, which forms red compounds in the presence of alkylamines or their quaternary bases, can be used successfully instead of acetone in reactions of polynitro-compounds (1,3,5-trinitrobenzene, picric acid). Bartos determined by this method many alkylamines and their hydrochlorides. Arylamines are less reactive and several hours are required for the appearance of the colour. The same workers [133] proposed a method for the photometric analysis of primary and secondary amines using 1-fluoro-2,4-dinitrobenzene and nitromethane in DMF. In order to obtain a more intense colour in solutions, Bartos introduced in addition potassium hydrogen borate. The addition of potassium hydrogen borate in DMF to the organic phase leads to an intense violet colour, a green-violet colour, and a green colour in the presence of primary alkylamines, secondary alkylamines, and aromatic amines respectively. The microanalysis of aromatic amines via the Janowsky reaction has been investigated [134] and its conditions have been discussed in detail.

It has been suggested that *sym*-trinitrobenzene be used for the determination of certain aromatic amines [135]. The authors regard this reaction as a charge-transfer process which leads to the formation of $\pi-\pi$ complexes absorbing in the ultraviolet or in the visible region, λ_{max} depending on the nature of the amine (primary, secondary, or tertiary). Thus aniline and toluidine (primary amines) can be readily distinguished from *N*-methylaniline (a secondary amine) and *N*,*N*-dimethyl- and *N*,*N*-diethyl-anilines (tertiary amines).

Legradi [136,137] suggested that aliphatic amines and amino-acids be determined with the aid of 2,4-dinitrobenzene in the presence of hydroxylamine hydrochloride as the catalyst. Obtemperanskaya and coworkers [138,139] also used 2,4- and 3,5-dinitrobenzenes to analyse primary and secondary aromatic and heterocyclic amines and hydrazines. The majority of aromatic primary amines and hydrazines are phenylated quantitatively at room temperature. The appearance and development of the colour of the solutions over a period of time and its stability depend on the nature of the functional substituents in the benzene ring of the amine or hydrazine. The sensitivity of the method is to within $10^{-5}-10^{6}$ M and the accuracy of the determination if to within 0.13–2.8% for aliphatic amines, 0.8–6.0% for aromatic amines, 0.5–4.7% for heterocyclic amines, and 0.6–4.0% for substituted hydrazines.

A method has been proposed for the photometric microdetermination of certain biogenic amines in the presence of amino-acids and amino-alcohols, based on the reaction with 3,5-dinitrobenzoyl chloride [140]. The sensitivity and accuracy of the method are to within 1×10^{-6} M and 2% respectively. The same workers used 2,4-dinitrobenzoyl chloride for the analysis of aromatic, aliphatic, and acyclic amines. The reaction takes place quantitatively at room temperature, its sensitivity and accuracy being to within 1.3×10^{-6} M and 0.2–2.8% respectively. Obtemperanskaya et al. [141] made a comparative assessment of 3,5-dinitrobenzoyl and 2,4-dinitrobenzoyl chlorides. The latter reagent is more sensitive and in addition can be used for a test in the qualitative analysis of aromatic, aliphatic, and acyclic amines, since it forms solutions having different colours. 1-Fluoro-2,4-dinitrobenzene can be employed successfully for the analysis of aromatic and aliphatic amines [142]. The reaction takes place quantitatively at room temperature for aliphatic amines and at 60°C for aromatic amines, its accuracy being to within 0.5–6.0%.

b. Determination using other chlorine-containing reagents. Fickentscher [143] and Tashima et al. [144] used chloranil (2,3,5,6-tetrachloro-1,4-benzoquinone) as the reagent for the photometric determination of nitrogen-containing compounds. On interaction with aromatic amines it gives rise to bluish violet solutions. Fickentscher determined by this method microamounts of dimethylamine in DMF; Tashima et al. [144] used this reagent for the analysis of methylcellosolve solutions of various aniline derivatives. The accuracy of the method is satisfactory.

Quinone dichloroimide has been proposed for the separate determination of aliphatic and aromatic amines [145]; 53 compounds have been studied by this procedure. The ability of many aromatic amines and heterocycles to react with polyhalogeno-compounds (with CBr_4 or CHI_3) and to give rise to coloured solutions under the influence of ultraviolet light served as the basis for their colorimetric analysis [146]. Apart from CBr_4 and CHI_3, di- and trichloroethylenes, hexachloroethane, and isopropyl iodide may be used; however, one should note that the method requires further development. There are several analytical procedures for hydroxylamines, including thin-layer chromatography [147,148].

Stewart and coworkers[149,150] proposed a new photometric method for the determination of microamounts of arylhydroxylamines with the aid of 9-chloroacridine. The sensitivity and accuracy of the method are to within 0.8 to 3.0 mg ml^{-1} and 1.6–3.6% respectively. Hydroxylamines can be determined by the same method in the presence of primary aromatic and aliphatic amines, amides, aromatic nitro-compounds, and phenols.

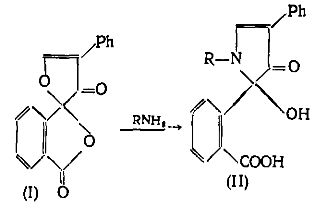
c. Determination using organic dyes. Organic bases and their salts may be determined by an extraction-photometric method using acid dyes as the reagents. The employment of dyes, whose solutions have high molar extinction coefficients, makes it possible to determine quantitatively amines in very dilute solutions. Two reviews[151,152], which discuss in detail the choice of dye and solvent, the influence of the pH of the medium, and the influence of various factors on the extraction constants of the complexes formed, have been devoted to the development of this method. A number of determinations have been made of the extraction constants[153–159]. It is recommended that Bromothymol Blue or the ethyl ether of tetrabromophenolphthalein be used for the analysis of quaternary ammonium salts[160,161]. Among all the solvents investigated, chloroform, a chloroform–alcohol mixture, or a benzene–isopentyl alcohol mixture proved to be most effective[162]. In the analysis of amines in the presence of Bromophenol Blue[163] the complexes formed were isolated and identified; the colour of the complex can be accounted for by the quinonoid structure of the dye. Bromophenol Blue, Bromocresol Purple, Bromocresol Blue, and Bromochlorophenol Blue have also been used as reagents for the determination of amines[164–167]. Korenman[164] used Bromophenol Blue for the quantitative determination of aromatic amines to within 0–6%.

Amines have been determined[165] by their extraction with chloroform using Bromocresol Purple and Bromothymol Blue. The authors established that the dyes react as singly-charged anions, which are responsible for the colour of the extracts of the amine compounds. The accuracy of the extraction-photometric analysis may be increased severalfold by adding C_1–C_4 alcohols to the reaction mixture[166] or by extraction with ternary nitrobenzene–chloroform–benzyl alcohol mixtures[167].

d. Determination of amines by the azo-coupling reaction. Azo-coupling is widely used for the determination of aromatic amines[3]. Diazotised dinitroaniline has been used[168] as a reagent for the determination of various aromatic amines; the reaction is carried out in highly acid solution and its accuracy is to within 0.5–5.9%. The method involving diazotisation with subsequent coupling to an H$^+$ acid and colorimetric determination of the resulting dye has been employed[169]; the authors determined toluidines, chloramines, and nitroanilines; the accuracy of the analysis is to within 1–1.5%. Bromonitrosol (3-bromo-2-nitroso-1-naphthol) can be used for the analysis of amines and hydrazines[170]; the reaction leads to the formation of coloured azo-compounds, which can be determined photometrically, but the accuracy of the analysis is comparatively low.

e. Other methods of colorimetric analysis. An interesting photometric method for the determination of *p*-phenylenediamine has been proposed by Corbett[171], its sensitivity and accuracy being to within 10^{-4}–10^{-5} M and 2% respectively. Aliphatic primary and secondary amines, α-amino-acids, sulphamides, hydrazines, and other compounds containing the amino-group condense in an alkaline medium with 1,2-naphthoquinone-4-sulphonic acid to form red, orange, and yellow derivatives of 1,2-naphthoquinonemonoimines[172]. The method is simple and highly sensitive, but suffers from limitations in the determination of secondary arylamines. The method involving the coulometric titration of amines is of definite interest[173]. Biphenyl radical-anions are used as the titrant. At a low rate of conversion it is possible to measure the absorption due to intensely coloured radical-cations generated from the amines in the course of the reaction; the accuracy is to within 1.7 to 3.0%.

Fluorescamine (I),[174] which forms coloured compounds (II) with amines, is an effective reagent in the colorimetric analysis of primary amines:



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The pH of the medium and the concentration of reagent (I) are important for the reaction. The sensitivity of the method is to within between 0.01 and 0.1. M.Legradi[175,176] used successfully phenylacetonitrile in an alkaline medium and diazotised sulphanilic acid for the analysis of nitro-compounds. The method described by Mordovina et al.[177] may be used for the microdetermination of nitrobenzenes in aqueous solution. Thiourea dioxide $(NH_2)_2CSO_2$ in an alkaline medium has been suggested for the microdetermination of the nitro-groups in aromatic compounds; the sensitivity of the method is high and its accuracy is to within 1–4%.

2. Photometric Analysis Using Inorganic Reagents

Quantitative photometric analytical methods, based on reactions with simple and complex metal salts, are widely used in the analysis of nitrogen-containing organic compounds[3]. Many fundamental studies devoted to a detailed investigation of the structures of the complex formed and the determination of various factors influencing the reaction have been published in recent years. For example, a study has been made[178] of 15 different aromatic amines in the presence of 13 metal ions[178]: Cr^{3+}, Cu^{2+}, Fe^{3+}, Bi^{3+}, Ag$^+$, Ni^{2+}, etc. It was shown that, in the presence of hydrogen peroxide and alkali, coloured complexes are formed and that the colour of the solution depends on the concentration of the amine. A method based on the reaction with $Fe(NO_3)_3$ in the presence of acetyl chloride is highly sensitive in the determination of aliphatic and aromatic amines[179]. The influence of temperature, the concentration of the salt and acetyl chloride, and the pH of the medium on the formation of the complexes has been studied, and a mechanism has been proposed for the formation of the complexes; the accuracy is to within at least 3%.

Connors and Albert[180] used successfully the Hamilton reagent for the analysis of 15 aromatic amines, including α-methylbenzylamine. The reaction with the copper(II) ion in ammonia solution has been used in the determination of isomeric aminophenols in mixtures[181]; the reaction led to the formation of coloured complexes, which were extracted with 1-butanol and determined colorimetrically. Copper and nickel salts in the presence of salicylaldehyde have been used to analyse amines[182]; the reaction results in the formation of coloured complexes: yellow for aromatic amines and yellow-green for aliphatic amines. Mitsui and Fujimura[183] used this method to determine primary amines but, instead of salicylaldehyde, they employed nitrosalicylaldehyde; the accuracy of the method is to within 0.5–1.5%.

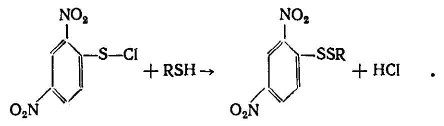
Legradi[184] developed an interesting drop method for the determination of amines and hydrazines with the aid of silver nitrate in the presence of alkalis; a drop of an ethanol solution of the amine (or hydrazine), a drop of silver nitrate solution, and a drop of 0.1 *N* NaOH are deposited on filter paper, which results in the appearance of an intense colour. This method may be used to determine *p*-, and *o*-phenylenediamines, *o*-aminophenol, anisidines, and toluidines. Sodium nitroprusside, which forms solutions with a characteristic colour, is fairly frequently used to determine amino-compounds[1,2]. Sodium nitroprusside was used comparatively recently[185] in a mixture with acetaldehyde for the quantitative determination of secondary aliphatic amines in a mixture with primary amines. The same method can be employed also for the determination of *N*-methylated amino-acids to within 3%. Marco and Mecarelli[186] used sodium nitroprusside together with ferrocyanate for the determination of guanidine and arginine derivatives. The employment of a mixed solvent containing isopropyl alcohol and water prevents the formation of insoluble deposits and gives rise to a high intensity of the colour of the solution.

Reactions involving oxidation by potassium peroxydisulphate, potassium hexacyanoferrate, potassium bromate, sodium perchlorate, etc. are frequently used in the photometric analysis of amines[187-189]. Korotkova and Noskov[189] used $K_3[Fe(CN)_6]$ as the oxidant for the determination of certain aromatic amines and, in order to establish the optimum conditions for the photometric determination, they employed the Box–Wilson mathematical experimental design method.

In conclusion, one should note that each of the methods described for the quantitative colorimetric determination of nitrogen-containing compounds has its advantages, disadvantages, and limitations. Certain methods are applicable only to the simplest representatives of compounds of the class indicated and are not applicable to more complex systems; in many instances difficulties arise in carrying out the experiment. However, sometimes the colorimetric method of analysis is the only suitable procedure among all the known methods of functional group analysis for compounds of the given class.

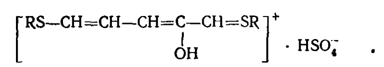
3. Photometric Analysis of Sulphur-containing Organic Compounds

Photometric methods for the determination of thiols are based on the following reactions: phenylation reactions, reactions with disulphides, and reactions with organomercury compounds. The first type includes primarily the dinitrophenylation reaction proposed[190] for the determination of aliphatic and aromatic thiols. The method proposed by the same workers[191] for the determination of thiols using 2,4-dinitrobenzoylsulphenyl chloride is based on the Janowsky and *sym*-phenylation reactions. The reaction of a thiol with an excess of the reagent by a factor of 2–3 is quantitative over a period of 3–5 min at 50°C:



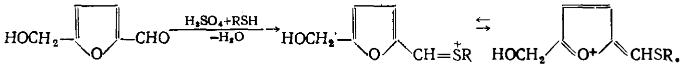
After the Janowsky reaction has been carried out, photometric measurements are made on the solutions at $\lambda = 480$ nm.

Another interesting reaction has been suggested by Unorits[192]. Furfural reacts with thiols in sulphuric acid at room temperature to form a red-violet substance ($\lambda_{max} = 505$ and 535 nm), which consists of the hydrolytically cleaved furan ring:

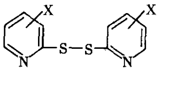


$$\left[RS{-}CH{=}CH{-}CH{=}\underset{\displaystyle OH}{\underset{|}{C}}{-}CH{=}SR\right]^{+}\cdot HSO_4^- \ .$$

In the reaction with hydroxymethylfurfural ring opening does not occur, and the colour arises as a result of the formation of cations having the following structure:

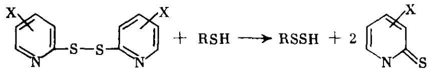


The use of heterocyclic disulphides of the type



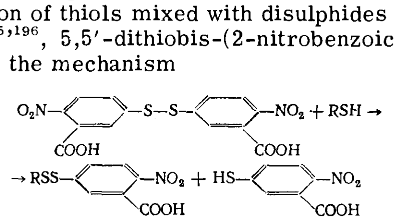
X = NO_2, NH_2, or COOH.

has been proposed for the photometric determination of thiols[193]. The reaction proceeds in accordance with the equation



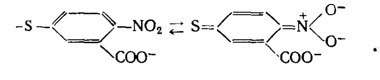
The thiopyridone formed absorbs in the range 240–430 nm. We may note that the accuracy of the method is low.

4,4′-Bisdimethylaminophenylmethanol, which forms intensely blue cations at pH 5.0, is also used as an alkylating agent[194]. The addition of a thiol causes the disappearance of the colour. This method is widely used in the analysis of proteins. Photometric methods for the determination of thiols mixed with disulphides have been described[195,196], 5,5′-dithiobis-(2-nitrobenzoic acid), reacting via the mechanism



(III)

being used as the reagent. An intense yellow colour ($\lambda_{max} = 412$ nm) arises owing to the formation of the aromatic mercaptide (III). The generation of the colour due to this mercaptide has been demonstrated by the detection of the quinonoid mesomeric structure



Reactions with organomercury compounds are widely used in photometry[64,196]. *p*-Dimethylaminophenylmercury acetate and *p*-diethylaminophenylmercury acetate are used for the extraction-photometric determination of thiols. It is suggested[64] that organomercury compounds form chelates with diphenylcarbazone which has a bright violet colour in benzene. The accuracy of the method is to within 4–8%; thioureas, sulphates, nitrates, and phosphates do not interfere with the determination. The results of the photometric method agree satisfactorily with those of titrimetric analysis where the given reagents are used as titrants.

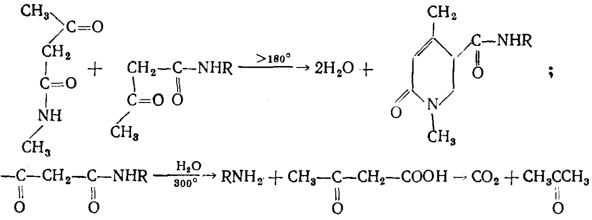
Only one paper has been published in the last six years on the photometric determination of sulphides and disulphides, involving the determination of thiuram disulphide in fungicides in the course of the analysis of industrial preparations; the method is based on the reaction with copper acetate[73]. Basic dyes of the type of rhodamine C, Acridine Orange, and Chrysandine [chrysoidine? (Ed. of Translation)] have been proposed as reagents for the determination of sulphonic acids[46,52]. Some of the main factors which determine the interaction between basic dyes and sulphonic acids are the pH of the medium and the concentration of acid. Quinone derivatives are used in the colorimetric determination of thiourea. Thus 1,4-diamino-5-nitroanthraquinone has been used in anhydrous acetic acid[200]; the measurements were made at 565 nm. Thioureas, thiosemicarbazides, monothiosemicarbazides, and isothiocyanates react with 2,3-dichloro-1,4-naphthoquinone in an ethanol solution of ammonia, forming an intense violet colour[201]. Apart from ammonia, pyridine, quinoline, ethylamine, and aniline may be used as the bases. The sensitivity of the method decreases in the sequence thiosemicarbazones > thiosemicarbazides ≫ thioureas > isothiocyanates. We believe that the method requires further development. Wronski[202] suggested a method based on the reaction of thiourea with an alkaline solution of *o*-(hydroxymercuri)benzoic acid with heating.

It has been noted that aromatic substituents increase while aliphatic substituents decrease the rate of desulphonation; tri- and tetra-substituted and cyclic thioureas are extremely resistant to this reaction. Attempts have been made[88,203] to reduce the reaction time by employing dipolar aprotic solvents—dimethylformamide and dimethyl sulphoxide. An interesting photometric method has been proposed for the determination of xanthates[204]: acetone and then the xanthate are added to a solution of nickel nitrate in acetic acid; photometric measurements are then made at 420 nm on the resulting intensely yellow solution. The error of the method is to within less than 0.5%. Dixanthates are determined with the aid of an excess of potassium thiocyanate[205]; the amount of potassium thiocyanate is determined photometrically on treatment with $(NH_4)_2SO_4.Fe(SO_4).24H_2O$ in nitric acid. A comparative assessment of all the methods for the analysis of sulphur-containing compounds permits the conclusion that the potentiometric titration procedures are the most suitable, being simplest and most accurate.

IV. OTHER METHODS

One should consider in the first place certain new analytical methods devised in recent years. A definite interest attaches to the method for the determination of aliphatic nitriles based on catalytic hydrogenation with subsequent titration in a non-aqueous medium[206]. The authors[206] devised a special apparatus for the hydrogenation of nitriles, which occurs in the presence of platinum oxide as the catalyst in acetic acid. The amines formed are determined by potentiometric titration with 0.1 *N* $HClO_4$ solution in dioxan. The standard deviations do not exceed 0.003–0.006.

Two methods for the determination of amides are noteworthy: the ion-exchange method[207] and analysis of *N*-substituted amides by the thermal cleavage method[208]. The latter procedure is based on brief (1–2 min) heating of amides at 300–400°C, amides being readily decomposed under these conditions to the amines and acids (or their decarboxylation products). The reaction products are identified chromatographically (by TLC or paper chromatography). More than one hundred compounds have been studied by this method; a mechanism has been proposed for the cleavage reaction and may be represented schematically as follows[208]:



$$CH_3-\underset{\underset{O}{\|}}{C}-CH_2-\underset{\underset{O}{\|}}{C}-NHR \xrightarrow[300^\circ]{H_2O} RNH_2 + CH_3-\underset{\underset{O}{\|}}{C}-CH_2-COOH \rightarrow CO_2 + CH_3\underset{\underset{O}{\|}}{C}CH_3 .$$

A highly sensitive colorimetric method[209], in which the amide group is oxidised with bromine, the excess bromine is decomposed by sodium formate and the products are oxidised further with iodine until the formation of a pale-blue complex (the "tri-iodine – starch" complex), may be used to determine trace amounts of various amides in aqueous solutions; photometric measurements are made on the complex at 610 nm. The accuracy of the method is to within 3.0%.

A rapid and convenient micro-gas-volumetric method for the determination of the hydrazino-group in organic and inorganic compounds by oxidation of the group with *p*-benzoquinone in 5% Na_2HPO_4 solution has been reported[210]. Hydrazine derivatives may be determined by this procedure in the presence of ammonium salts; the accuracy is to within 0.2%. A method for the quantitative determination of dimethylhydrazine in solution by classical and a.c. polarography has been developed recently[6]. The method may be used in the dimethylhydrazine concentration range 10^{-3}–10^{-6} M and the error is 4%.

A very interesting analytical method has been developed for the determination of a mixture of α-amino-alcohols (primary, secondary, and tertiary) by treatment with an excess of potassium periodate in a weakly alkaline medium[211]. The method is rapid and accurate; the presence of α-amino-acids and α-diamines does not interfere with the analysis. It should also be mentioned that, following the development of the technique of ion-selective electrodes[213,216], potentiometric methods have come to be even more widely used for the determination of various nitrogen and sulphur-containing compounds. These methods may be used to determine many substances belonging to the classes noted above[5,6,212,214,215]. The polarographic method is used on a fairly wide scale in the analysis of complex organic sulphur-containing compounds[5,198].

The experimental data presented in this review indicate the great interest of investigators in the problem of the functional group analysis of nitrogen- and sulphur-containing organic compounds. At the same time one should note that there are still too few universal methods for the chemical analysis of mixtures of compounds belonging to different classes. The problems to be solved in the immediate future apparently involve the search for new reagents and greater use of mathematical experimental design methods for the selection of optimum reaction conditions.

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During the preparation of the manuscript for the press, a number of new publications appeared. There are several reviews devoted to general problems of functional group analysis[217-220]. Titrimetric methods for the determination of nitrogen- and sulphur-containing compounds have been described[221-225] and accounts of photometric methods have appeared[256-266]. Other analytical methods have also been described[267-281].

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Packed Capillary Columns in Gas Chromatography

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Data on the preparation, properties, and applications of packed capillary columns are surveyed and analysed. The characteristics of chromatographic separation in columns of this type are discussed, the principal ways of improving the efficiency of packed capillary columns are considered, and the regions where they can be employed in practice are indicated.
The bibliography includes 85 references.

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I. INTRODUCTION

One of the methods for improving the efficiency of separation in gas chromatography involves the use of small-diameter columns. The first capillary column was proposed by Golay[1] and many different useful modifications of small diameter columns, whose advantages have been demonstrated quite clearly in recent years, are now known. However, there are no reviews in the literature on packed capillary columns, which inhibits somewhat their wide-scale application.

Packed capillary columns (PCC) should be understood as columns having an internal diameter $\leqslant$ 2 mm and filled with a sorbent. This definition is arbitrary and somewhat subjective, owing to the absence of a clear-cut boundary between packed capillary columns and ordinary packed columns. According to our observations, characteristic features begin to be manifested precisely in columns whose diameter is 1–2 mm. The above definition indicates the upper limit of the diameter. Most studies have been carried out on columns having diameters less than 1 mm.

Halasz and Heine[2] obtained the first PCC by drawing on a Desty machine[3] tubes which had been filled either with an active adsorbent[2,4-8] or with an inert carrier[9], the stationary phase being deposited subsequently on the latter by the frontal method. The distribution of the sorbent is non-uniform in columns obtained by this procedure; it is partly forced into the walls of the capillary. This method can be used to obtain long columns with a comparatively high efficiency, but a carrier with an adequate mechanical strength and thermal stability is required; in most cases the carrier cannot be treated with the stationary phase beforehand. Capillary columns with regular close packing of the sorbent, obtained[10] by filling 200 cm steel tubes having internal diameters of 0.25 and 0.5 mm with glass microbeads (grain size 40 μm) and depositing on the latter the stationary liquid phase (SLP) by the frontal method, proved to be preferable. The height H of columns obtained in this way equivalent to the theoretical plate was 2 and 0.7 mm. More efficient columns ($H = 0.3$–0.39 mm) were obtained subsequently in a study[11] where metallic columns 0.5 and 1 mm in diameter and 100 cm long were filled with Chromosorb or Kieselguhr by means of a vibrator, and then the SLP was again deposited on the solid carrier in the column by the frontal method.

Capillary columns filled with the sorbent prepared beforehand have been used in gas-chromatography since 1963.[12-17] Systematic study of the characteristics of columns of this type have also been carried out in other investigations[18-25] dealing with broader aspects of their general analytical properties (in particular, a study was made for the first time of the changes in the efficiencies of columns of this type as a function of the principal experimental parameters) and their usefulness for the measurement of physicochemical characteristics was demonstrated.

In the development of sorbent-filled capillary columns, it is possible to distinguish two stages: (1) the development of methods for the preparation and application of short columns; (2) the development of methods for the preparation and application of long columns. Short columns (mainly 1–2 m long) are characterised by a high specific efficiency (the number of theoretical plates per metre of column length is approximately 2000), but their overall efficiency is small (usually not more than 2000–5000 theoretical plates). Short columns can be usefully employed for rapid analysis of relatively simple mixtures. The second stage, involving the development of long packed capillary columns (more than 10 m long) did not begin until 1971.[26] The high efficiency of these columns (columns with an efficiency equivalent to 60 000 theoretical plates have been described, but even longer columns can be prepared) makes them useful for the investigation of multicomponent mixtures and mixtures which are difficult to resolve and for the analysis of impurities.

Owing to their low diameter and the presence of the sorbent, PCC combine the advantages of classical capillary columns (capillaries whose internal walls are coated by the SLP) and ordinary packed columns. The small diameter is responsible for the significant advantages of PCC compared with columns of the usual type; these are (1) high efficiency, (2) high speed of the analysis (calculations[27] have shown that the time required for the attainment of the same degree of separation in PCC is shorter by a factor of two than in ordinary columns), (3) more stable conditions when the temperature is programmed owing to the low thermal inertia of the columns, (4) miniaturisation of the columns, i.e. the possibility of devising apparatus of small size, with a compact thermostat, in which rapid heating and cooling of the column may be achieved, and (5) low cost, i.e. there are extensive possibilities for employing scarce and expensive sorbents, since the amounts required are small. The following disadvantages of PCC compared with ordinary packed columns may be mentioned: (1) the filling technique is somewhat more difficult and prolonged and (2) it is necessary to employ detectors with a "dead" volume less than 30 μl, particularly a microkatharometer, since an ordinary katharometer cannot be used owing to its high inertia[28].

Because of the use of a sorbent in PCC, the latter have many advantages compared with classical capillary columns: (1) a high rate of separation of readily and moderately sorbed substances[27]; thus the time for separation in PCC is shorter by a factor of approximately 30 for a partition coefficient $K = 10$ and by a factor of 2.3 for $K = 50$; (2) by employing sorbents of different polarity, one can prepare columns of this type with a high selectivity for both gas–liquid and gas–solid chromatography; (3) a fairly high capacity, which makes it possible to introduce the sample without dividing the stream and thus reduces the error in the qualitative results and makes the requirements for the sensitivity of the detector less stringent (experiments with a microkatharometer are possible). Furthermore, it leads to an increase of the separating capacity of the column in the separation of weakly sorbed substances and extends the scope of capillary chromatography in the analysis of admixtures. A deficiency of PCC compared with classical capillary columns is a fairly high resistance to flow.

Comparison of PCC characteristics with those of columns of the type usually employed shows that their wide-scale application in chromatographic practice is entirely justified.

II. CHARACTERISTICS OF THE CHROMATOGRAPHIC SEPARATION PROCESS IN PACKED CAPILLARY COLUMNS

Theoretical and experimental studies designed to elucidate the dependence on column diameter of the spreading of the chromatographic band in narrow columns have been carried out for gas-liquid chromatography[27,29] and gas-adsorption chromatography[27,30,31], where the fundamental efficiency characteristics were adopted as the spreading criteria, namely the minimum height equivalent to the theoretical plate ($H_{\min}$) and the coefficient of resistance to mass transfer (C) in the Van Deemter equation[32]:

$$H = A + \frac{B}{u} + Cu,$$

where A and B are coefficients taking into account the turbulent and molecular longitudinal diffusion respectively and u is the carrier gas flow rate.

Comparative results for the efficiency of packed columns of different diameters (Table 1)[27] show that in gas-liquid chromatography (GLC), $H_{\min}$ changes insignificantly in columns 1.2, 0.8, and 0.5 mm in diameter and increases appreciably only in a column with a diameter of 3 mm. According to other workers[29], an appreciable influence of column diameter (d_c) on $H_{\min}$ was not observed either in columns having diameters of 0.75, 1.0, and 1.5 mm. The coefficient of resistance to mass transfer C, which decreases with decrease of d_c (Table 1), changes more significantly. This type of behaviour has been observed for all the substances tested and for all carrier gases.

In gas-adsorption chromatography (GAC) a change in d_c has been found to entail, as in GLC, only slight changes in $H_{\min}$, the minimum value of $H_{\min}$ being obtained for the column 0.8 mm in diameter (Table 1). With decrease of the column diameter from 3 to 0.5 mm, the coefficient C diminishes almost by a factor of 2, and, compared with the column 0.8 mm in diameter, by a factor of approximately 2.5.

Fig. 1 presents the dependence of C on the column diameter d_c.

In GLC C decreases monotonically with decrease of d_c. In GAC the curve relating C to d_c passes through a minimum. This difference can apparently be accounted for by the different grain sizes of the sorbent employed: a coarser sorbent (100–200 μm) is used in GAC than in GLC (100–160 μm), so that in a 0.5 mm diameter column (GAC) the sorbent was probably more loosely packed, which led to an increase in the degree of spreading.

Earlier studies[30,31] on GAC showed a somewhat different variation of $H_{\min}$ with d_c: in the range d_c = 1.6–0.6 mm the quantity $H_{\min}$ is directly proportional to d_c, increasing as d_c is diminished further (on passing from 0.6 to 0.3 mm).

Table 1. The influence of the diameter of the column on its efficiency.

Method	d_c, mm	$H_{\min}$, mm		u^*_{opt}, cm s^{-1}		10^2C, s		$H_{\min}$, mm		u^*_{opt}, cm s^{-1}		10^2C, s		$H_{\min}$, mm		u^*_{opt}, cm s^{-1}		10^2C, s	
		nitrogen	helium	nitrogen	helium	nitrogen	helium	nitrogen	helium	nitrogen	helium	nitrogen	helium	nitrogen	helium	nitrogen	helium	nitrogen	helium
		Pentane						Hexane						Octane					
GLC	3.0	0.52	0.88	6.0	7.0	1.5	1.25	0.54	0.78	5.0	7.5	1.3	1.00	0.60	0.72	5.0	8.5	1.10	0.70
	1.2	0.46	0.60	8.0	9.5	0.8	0.64	0.46	0.62	6.0	11.0	0.76	0.50	0.52	0.60	6.5	11.0	0.70	0.44
	0.8	0.42	0.60	8.0	9.5	0.66	0.48	0.45	0.58	8.0	11.0	0.60	0.44	0.48	0.55	6.0	11.0	0.56	0.34
	0.5	0.41	0.60	8.0	9.5	0.48	0.36	0.44	0.58	8.0	11.0	0.46	0.32	0.48	0.55	6.0	11.0	0.44	0.26
GAC	3.0	0.40	0.42	4.5	7.0	1.10	0.70	0.45	0.46	4.0	7.0	1.05	0.60	—	—	—	—	—	—
	1.2	0.40	0.40	5.0	8.0	0.70	0.50	0.42	0.52	5.0	8.0	0.65	0.42	—	—	—	—	—	—
	0.8	0.28	0.32	5.0	8.0	0.40	0.28	0.32	0.35	5.0	9.0	0.33	0.25	—	—	—	—	—	—
	0.5	0.38	0.50	6.0	9.0	0.50	0.36	0.40	0.55	5.0	9.0	0.48	0.34	—	—	—	—	—	—

---

*The optimum rates u_{opt} are quoted.

The relations obtained[27,29-31] between the efficiency of the columns and their diameters are in the main analogous. Certain discrepancies in the optimum column diameters (0.8 mm[27] and 0.6 mm[30,31]) can probably be explained by the different grain sizes of the sorbents used.

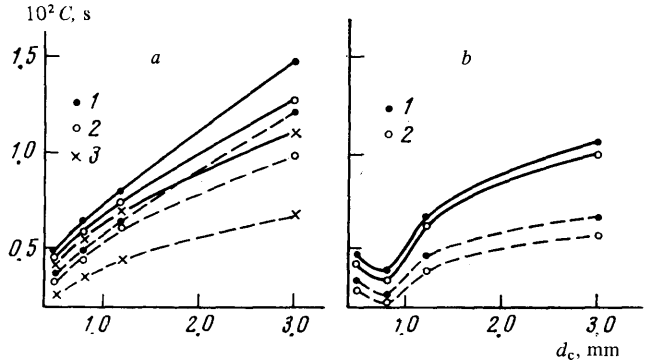

Figure 1. Dependence of the coefficient of resistance to mass transfer C on the column diameter d_c: a) sorbent—5% of squalane on Chromosorb W (100–160 μm); b) sorbent–XOB.075 Spherosil (100 – 200 μm); 1) pentane; 2) hexane; 3) octane. Continuous lines—nitrogen as carrier gas; dashed lines—helium as carrier gas.

According to the Jones equation[33]

$$H = A + \frac{B}{u} + C_g u + C_s u,$$

kinetic spreading in the chromatographic process is due to the resistance to mass transfer in the mobile (C_g) and stationary (C_s) phases. According to the Giddings theory[34], each of these factors plays a significant role in the assessment of the spreading mechanism in the column. In the study of the spreading of a chromatographic band in PCC it is therefore of interest to investigate the question of the relative role of mass transfer in the mobile and stationary phases as a function of d_c. Such studies were made for the first time for GLC[25] and their authors proposed a graphical method for the separate determination of the coefficients of external diffusion and internal diffusion resistance to mass exchange, and estimated their contributions as a function of the ratio of d_c to the grain diameter d_p. The coefficients of the external diffusion resistance to mass transfer C_g for a column 0.58 mm in diameter increase only slightly with increase of d_p. For a column with a larger diameter (0.98 mm) and for the same ratios d_c/d_p, the quantity C_g is greater by a factor of two and an increase of d_p by a factor of ten leads to an increase of C_g also by a factor of ten.

The results of a recent separate determination of C_g and C_s in GLC and GAC[27] by the method described in Grant's book[35] are presented in Table 2. Evidently both C_g and C_s diminish with decrease of d_c, the values of C_s found by two other methods (described by Perrett and Purnell[36] and Novak et al.[37]) being in good agreement. The changes observed[27] in C_s conflict with the classical concept of the independence of processes controlling the interphase mass transfer in a chromatographic column and agree with the conclusions of Novak and coworkers[37,38], who showed theoretically and experimentally that the coefficients C_s and C_g depend on each other and on the average pressure in the column. In the case considered the average pressure increases with increasing column diameter, which may be accounted for by the increase of permeability in narrow columns (for $d_p/d_c > 0.05-0.1$)[39], apparently owing to the greater influence of the wall effect.

Table 2 also shows that in gas–liquid chromatography $C_s > C_g$ for pentane in all the columns investigated, the difference diminishing on passing to substances with larger extraction coefficients. In gas-adsorption chromatography $C_g > C_s$ for a column 3 mm in diameter; for the other columns investigated the values of these quantities are comparable (when nitrogen is used as the carrier gas).

The dependence of C_g on d_c is illustrated in Fig. 2. The power exponent m in the relation $C_g \propto d_c^m$, found from the slopes of the straight lines, is 0.42 for GLC and 0.8 for GAC; this difference has been explained[27] as the influence of the form of the sorbent and the grain size on its packing in columns of different diameters.

The greater efficiency of PCC compared with packed columns having the usual diameters is apparently due to the special role of radial diffusion in the spreading of the band in PCC[30] and the nature of the packing of the sorbent in them[27]. In order to test the hypothesis of the greater smoothing role of radial diffusion in narrow columns, a comparative study has been made[40] of the efficiencies of capillary and the usual packed columns filled with a sorbent known to be inhomogeneous (mixed), which consisted of a mixture of a sorbent for GLC (i.e. of particles of the solid

Table 2. The coefficients of resistance to mass transfer in the mobile (C_g) and stationary (C_s) phases.

Method	d_c, mm	$10^2 C$, s		$10^2 C_g$, s		C_s	$10^2 C$, s		$10^2 C_g$, s		C_s	$10^2 C$, s		$10^2 C_g$, s		C_s
		nitrogen	helium	nitrogen	helium		nitrogen	helium	nitrogen	helium		nitrogen	helium	nitrogen	helium	
		Pentane					Hexane					Octane				
GLC	3.0	1.5	1.25	0.33	0.130	1.12	1.30	1.00	0.45	0.15	0.85	1.10	0.70	0.57	0.16	0.53
	1.2	0.8	0.64	0.24	0.034	0.56	0.76	0.60	0.30	0.10	0.46	0.70	0.56	0.37	0.11	0.33
	0.8	0.66	0.48	0.21	0.073	0.45	0.60	0.44	0.24	0.03	0.36	0.56	0.34	0.31	0.09	0.25
	0.5	0.48	0.36	0.18	0.063	0.30	0.46	0.32	0.21	0.07	0.25	0.44	0.26	0.25	0.075	0.19
GAC	3.0	1.10	0.70	0.61	0.21	0.49	1.05	0.60	0.67	0.23	0.33	—	—	—	—	—
	1.2	0.70	0.50	0.30	0.10	0.40	0.65	0.42	0.36	0.12	0.30	—	—	—	—	—
	0.8	0.40	0.28	0.18	0.06	0.22	0.33	0.25	0.18	0.06	0.19	—	—	—	—	—
	0.5	0.50	0.36	0.21	0.07	0.29	0.48	0.34	0.21	0.07	0.27	—	—	—	—	—

carrier impregnated with the SLP) and the solid carrier without SLP. The measurements were performed on two spiral columns: a glass column 3 m long and with an internal diameter of 0.8 mm, and a metallic column 2.9 m long and with an internal diameter of 3 mm. The two columns were filled with the same sorbent, which consisted of a mixture of Chromaton N-AW without an SLP, and Chromatone N-AW with 5% of squalane in different proportions: 95 and 5, 50 and 50, and 0 and 100 wt.% respectively.

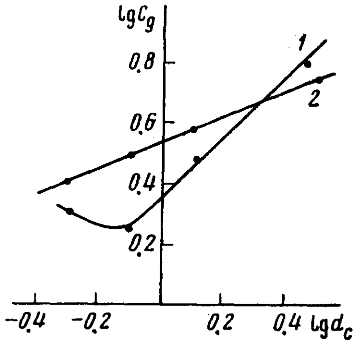

Figure 2. Dependence of the coefficient of resistance to mass transfer in the mobile phase C_g on column diameter d_c: 1) GAC; 2) GLC.

Table 3. The efficiency of columns having different diameters and filled with a mixed sorbent[40].

Sorbent, %		d_c, mm	10^2C, s			H_{min}, mm		
Chromaton + 5% of squalane	Chromaton N-AW		heptane	toluene	octane	heptane	toluene	octane
5	95	3.0	2.2	2.2	4.6	1.3	1.7	1.6
5	95	0.8	1.6	1.7	3.0	1.1	1.4	1.3
50	50	3.0	2.0	1.9	1.8	1.1	1.0	1.0
50	50	0.8	1.5	1.5	1.4	1.0	0.9	0.9
100	0	3.0	1.1	1.0	1.0	0.9	0.7	0.8
100	0	0.8	0.9	0.8	0.8	0.8	0.7	0.7

It follows from the results presented in Table 3 that, for all the substances investigated which are characterised by different partition coefficients, the values of H_{min} and C are smaller for the capillary column. They diminish (i.e. the efficiency improves) with decrease of the inhomogeneity of the sorbent. We may note that the greatest decrease of H_{min} and C is observed on passing from the packing containing 5% of the sorbent to the packing containing 50% of the sorbent, i.e. in the region of the greatest increase of the inhomogeneity of the sorbent. The experimental results are fully consistent with the idea that radial diffusion plays an important smoothing role in PCC. Indeed the time required for the diffusion of the molecules of the substance analysed in the gas phase from one wall of the column to the other may be estimated from the equation:

$$\tau = d_c^2/2D, \qquad (1)$$

where D is the diffusion coefficient of the test substance in the gas phase. If it is assumed that $D = 0.5$ cm^2 s^{-1}, then we have $\tau = 6.4 \times 10^{-3}$ s for a capillary column 0.8 mm in diameter and $\tau = 9 \times 10^{-2}$ s for an ordinary packed column 3 mm in diameter, i.e. τ is 15 times longer (the influence of the tortuosity of the path was disregarded in this calculation).

Thus, when a mixed sorbent is used, the efficiency of PCC is in all cases greater than that of large-diameter columns; the relative improvement of the efficiency characteristics of PCC increases with increasing inhomogeneity of the sorbent.

The equalisation of the chromatographic band front over the cross-section of PCC and an ordinary analytical column has been studied qualitatively[27]. The shape of the boundary of the layer of sorbent saturated by the volatile component, which reacts chemically with the sorbent to form a coloured compound, was observed. The saturated (spent) layer was obtained as a result of the reaction of hydrogen sulphide with the sorbent—Chromaton N (125–160 μm), on the surface of which 3% of lead acetate has been deposited. The reaction results in the formation of black lead sulphide. Glass tubes 3 and 0.8 mm in diameter, filled with the above sorbent, were used in the investigation. Hydrogen sulphide was injected into the carrier gas directly at the column wall and at right angles to the stream. When hydrogen sulphide was introduced, the sorbent turned black. It was observed that the boundary of the front of the saturated sorbent forms an acute angle γ with the wall at which hydrogen sulphide has been injected.

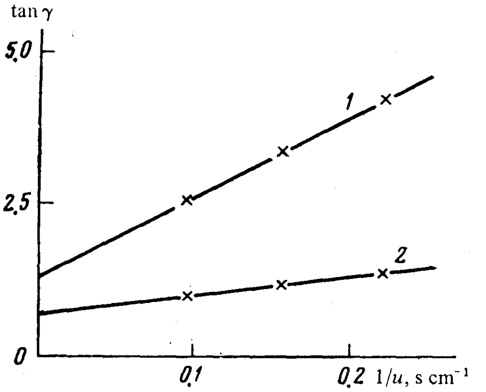

Figure 3. Dependence of the slope of the boundary of the saturated (spent) sorbent layer on the reciprocal of the linear carrier gas flow rate for columns having diameters of 0.8 mm (line *1*) and 3 mm (line *2*).

It follows from the data in Fig. 3 that, in a column 0.8 mm in diameter, the slope of the front for all the carrier gas flow rates investigated is greater than in an ordinary column 3 mm in diameter, i.e. the front of the band in PCC is steeper. This can probably be accounted for by the more regular packing of the sorbent in PCC. The time required for the diffusion in PCC of weakly sorbed molecules over a distance equal to the column diameter is $d_c/\tan\gamma \times u \simeq 4.5 \times 10^{-3}$ s, which agrees fully with the value calculated by Eqn. (1): $\tau = 6.4 \times 10^{-3}$ s.

One can apparently postulate the formation in packed columns of "domains"—regions of close-packed particles forming poorly ventilated cavities. It may be that the probability of their formation in PCC as well as their dimensions are much smaller, which should lead to a decrease of the spreading of the front. Furthermore, the effect of "remote" channels, noted by Giddings[34] as the main factor influencing the non-uniformity of the distribution of velocities with respect to the cross-sections of packed columns, should be significantly reduced in columns with small diameters, since it operates over fairly long distances, amounting to approximately $7.5d_p$, which is less than the diameters of the columns considered. Thus the non-uniform distribution of velocities with respect to the column cross-section plays a smaller role in PCC in the impairment of the efficiency characteristics than in columns having the usual diameters.

The characteristics of the separation in PCC, distinguishing them from classical capillary columns, are determined mainly by the presence of the sorbent in the former, which leads to a decrease of the phase ratio β (the ratio of the volume of the gas phase to that of the liquid phase in the column). β has a significant influence on separation. According to the equation[41]

$$R=\frac{\alpha-1}{4\alpha}\,\frac{K}{\beta+K}\,N^{1/2}$$

(R is the degree of separation, K the partition coefficient, N the number of theoretical plates, and α the relative retention volume), an increase of β should lead to an impairment of separation, which has a particularly marked effect in the separation of poorly sorbed compounds. Calculations have shown[40] that the amount of liquid phase in PCC is greater by two orders of magnitude than in classical capillary columns, and β is therefore much smaller.

The presence of the sorbent in PCC is also responsible for a different spreading mechanism than in classical capillary columns. The main characteristics of classical capillary columns are the absence of turbulent diffusion and a dependence of the coefficient of resistance to mass transfer in the gas phase mainly on dynamic diffusion. The coefficient C_s in classical capillary columns is usually greater than in PCC, since the film of the SLP on the porous sorbent is usually thinner than on the walls of capillaries. However, there have been no experimental studies of the comparative characteristics of spreading in PCC and classical capillary columns.

III. THE INFLUENCE OF THE PRINCIPAL EXPERIMENTAL PARAMETERS ON COLUMN EFFICIENCY

1. The influence of Pressure

One of the ways of increasing the overall efficiency of chromatographic columns involves increasing their length. Small PCC are promising in this respect. However, the increase in length entails an increase in the resistance of the columns, which leads to the necessity of employing increased pressures at the inlet to the column. For this reason, it is useful to examine the problem of the dependence of the efficiency of PCC on pressure.

The variation of the efficiency of the chromatographic column on various process parameters can be most fully described by the equation[29]

$$H_i=a_d\frac{D_{im}}{\bar u}+\frac{a_c'd_p}{1+a_e''(D_{im}/\bar u d_p)^{1/2}}+a_f\left(\frac{\bar u}{D_{im}}\right)^{1/2}d_p^{3/2}\left(\frac{k_i}{k_i+1}\right)^2+ \\ +a_b\frac{\bar u}{D_{ip}}d_p^2\frac{k_i}{(k_i+1)^2}, \qquad (2)$$

where H_i is the value of H for the ith component, $\bar u$ the average linear flow rate, D_{im} the diffusion coefficient for the ith component in the mobile phase, k_i the partition coefficient of the ith component, D_{ip} the overall diffusion coefficient of the ith component in a particle, and a_d, a_c', a_e'', a_f, and a_b are factors reflecting the influence of the geometry of the column on the diffusional and convective mixing, the dispersion caused by the mass exchange in the moving part of the mobile phase, and the dispersion caused by mass exchange in the particle, both in the "stagnant" component of the mobile phase and in the SLP. The diffusion coefficient in the mobile phase is related to pressure by the following equation:

$$D_{im}p=\text{const}, \qquad (3)$$

where p is the pressure.

It follows from Eqns. (2) and (3) that H decreases with increase of pressure for low linear flow rates and increases for high linear flow rates, the latter effect diminishing with decrease of d_p and k. In addition, as the pressure increases, the minimum value of H falls and shifts towards lower linear flow rates. The experimental results (Fig. 4)[27] show that this relation is characteristic of PCC in both gas–liquid and gas–adsorption chromatography. Huber et al.[29] obtained a detailed theoretical explanation of the results on the basis of Eqns. (2) and (3). With increase of pressure, the first term of Eqn. (2) diminishes, the second hardly changes in the usual range of flow rates, and the third increases. The influence of pressure on the fourth term of Eqn. (2) depends for its effect on D_{ip}, which in its turn depends on the degree of saturation of the pore space of the particles. In the simplest case the pores are completely filled by one phase, whereupon D_{ip} is proportional to the diffusion coefficient in this phase[42-45]. In gas–liquid chromatography the particles are usually saturated by the stationary liquid and the "stagnant" carrier gas. In this case the influence of pressure on D_{ip} is determined by the ratio of the volumes of the stationary liquid and gas phases in the particle and their relative geometrical distribution. With increase of pressure, the fourth term of Eqn. (2) increases and its value depends on the porosity of the particles, the accessible internal volume of which is filled by the stationary carrier gas.

According to the data of Bruner et al.,[46] $H_{\min}$ in gas–liquid PCC is independent of column length and hence of pressure (at least up to 15 m). For PCC of the gas–liquid–solid type, these workers observed, as in their first study[47], a "deepened" minimum on the curve relating H to u for comparatively long columns, i.e. with increase of the rate above u_{opt}, H initially increases, and then remains virtually unchanged. The authors suggest this effect may be caused by the mechanism of the operation of columns of this type.

The pressure gradient in the chromatographic column determines the presence of gradients of linear flow rates of the gas phase and of the diffusion coefficient in the mobile phase (owing to the high compressibility of the gas). The first three terms of Eqn. (2) remain constant, since the ratio D_{im}/u does not change. The influence of the pressure gradient on H is determined exclusively by the fourth term, describing the mass exchange in the particle. This term increases with increasing linear flow rate, which increases along the column as a function of the ratio of the inlet and outlet pressures[48]:

$$u_x = u_L \left\{\left(\frac{p_i}{p_0}\right)^2 - \left[\left(\frac{p_i}{p_0}\right)^2 - 1\right]\frac{x}{L}\right\}^{-\frac{1}{2}}, \tag{4}$$

where L is the column length, u_{L} the linear flow rate at the end of the column, x the coordinate along the length of the column, and p_{i} and p_0 are the pressures at the inlet and outlet.

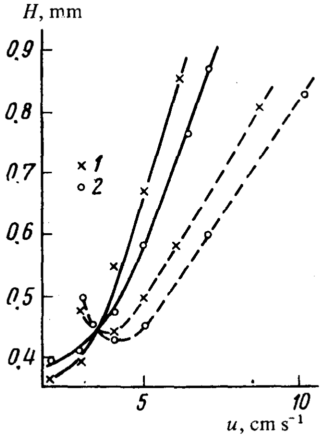

Figure 4. Dependence of H on the average linear carrier gas flow rate for short and long columns with an internal diameter of 0.8 mm, using 15% of squalane on Chromosorb P as the sorbent (100–160 μm) at 80°C: 1) hexane; 2) heptane. Continuous lines—15 m column; dashed lines—2 m column.

It follows from Eqns. (2) and (4) that H increases from the beginning to the end of the column in accordance with the expression

$$H_{ix} = \mathrm{const} + a_b \frac{u_L}{D_{ip}\left\{\left(\frac{p_i}{p_0}\right)^2 - \left[\left(\frac{p_i}{p_0}\right)^2 - 1\right]\frac{x}{L}\right\}^{1/2}} \cdot d_p^2 \frac{k_i}{(k_i+1)^2}, \tag{5}$$

where $H_{\mathrm{ix}} = H$ at the position defined by x. Eqn. (5) does not allow an exact prediction of the H_{i} gradient in the column, since D_{ip} is an unknown function of x.

Experimental results[27,29] have shown that the efficiency of PCC depends only slightly on the pressure gradient; the average pressure in the column has a much greater influence on the efficiency.

2. The Influence of the Particle Size of the Packing

The permeability of the column and to a large extent its efficiency depend on the particle size of the packing. Theoretically the permeability of an open capillary depends only on its diameter, but in practice the permeability of a capillary is smaller by 10–13% than the theoretical values r_0^2,[49] which can probably be accounted for by the roughness of the walls or fluctuations in the tube diameter. The permeability P of packed columns depends on the particle size and on the packing density[50,51]:

$$P = \frac{\psi^2 d_p^2}{180} \cdot \frac{\varepsilon_0^3}{(1-\varepsilon_0)^2},$$

where ψ is the particle inhomogeneity factor and ϵ_0 the column porosity, which does not include the internal volume of the particles. In practice the permeability of packed columns depends on the ratio of the particle diameter to the column diameter ($d_{\mathrm{p}}/d_{\mathrm{c}}$) and on the degree of roughness of the carrier. The permeability of the usual packed columns, where $d_{\mathrm{p}}/d_{\mathrm{c}} < 0.1$, is independent of the column diameter[52].

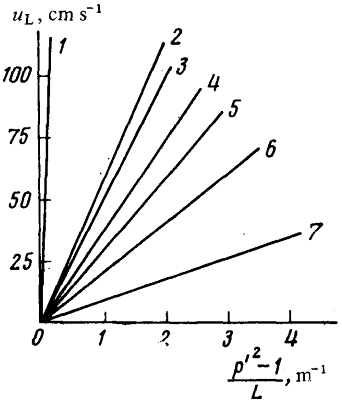

Figure 5. Dependence of the carrier gas flow rate at the outlet u_{L} on $(p^2 - 1)/L$ for columns of different types: 1) classical capillary column (internal diameter 0.25 mm); 2) and 4) PCC, $d_{\mathrm{p}} = 100 - 125$ μm, $d_{\mathrm{c}} = 0.45$ and 0.55 mm respectively with Chromosorb P as the carrier; 3) and 5) PCC, $d_{\mathrm{p}} = 140 - 160$ μm, $d_{\mathrm{c}} = 0.64$ and 1.26 mm respectively with glass beads as the carrier; 6) and 7) usual packed columns, $d_{\mathrm{p}} = 200$–250 μm and $d_{\mathrm{c}} = 4$ mm with glass beads as the carrier.

The column permeability may be determined experimentally from the slope of the plot of the linear carrier gas flow rate at the outlet of the column u_{L} against $(p'^2 - 1)/L$:

$$u_L = \frac{P p_0 (p'^2 - 1)}{2\eta L},$$

where η is the viscosity of the carrier gas, p_0 the pressure at the outlet from the column, $p' = p_{\mathrm{i}}/p_0$, and p_{i} the pressure at the inlet. Plots of this relation for different types of column are illustrated in Fig. 5.[52] Evidently the permeabilities of PCC occupy an intermediate position between those of classical capillary columns and ordinary packed columns; for a given particle size, the permeability diminishes with increase in column diameter. Cramers et al.[53] showed that a decrease of the column diameter with the same grain size of the packing requires the application of lower pressures at the inlet to the column (Fig. 6). Rijks et al.[54] recommend the ratio $d_p/d_c = 0.2-0.25$ for the optimum permeability of PCC.

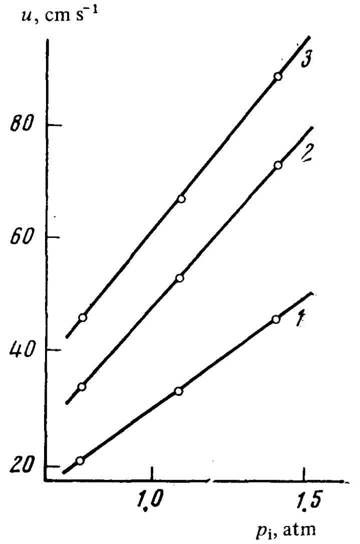

Figure 6. Dependence of u on the inlet pressure p_i for 1 m columns with different diameters (mm): 1) 1.26; 2) 0.92; 3) 0.64.

It has been shown[29] that a decrease of d_p leads to the following changes in the efficiency of PCC: (1) $\bar{H}_i$ diminishes for low values of $\bar{u}$; (2) the limiting value of $\bar{H}_i$, obtainable at high values of $\bar{u}$, diminishes for non-retained compounds; (3) the minimum value of $\bar{H}_i$ for retained compounds shifts towards lower values and its magnitude is greatly diminished; (4) the slope of the right-hand branch of the plot of $\bar{H}$ against $\bar{u}$ decreases for retained compounds. These experimental results have been explained[29] on the basis of Eqn. (2). With atmospheric pressure at the inlet the changes in $\bar{H}_i$ are induced directly by the change in d_p in Eqn. (2) and by the indirect influence of size owing to the dependence of the pressure drop on d_p (p' increases with decrease of d_p for a given value of $\bar{u}$). When the pressure at the outlet is increased, p' increases only slightly with decrease of d_p for a given value of u. In this case the changes in $\bar{H}_i$ are caused mainly by the change in d_p in Eqn. (2). The decrease in the minimum value of $\bar{H}_i$ for retained compounds and the decrease of the limiting value of $\bar{H}_i$ for high values of $\bar{u}$ for non-retained compounds, as well as the decrease of the slope of the curves relating $\bar{H}$ to $\bar{u}$ for retained compounds at high values of $\bar{u}$ are caused directly by the decrease of d_p in Eqn. (2). Thus the decrease of the particle size of the packing has a favourable influence on the column efficiency.

Generalising the results obtained, Huber et al.[29] concluded that PCC filled with a packing having particles much smaller than usual may prove to be extremely effective. The columns which they prepared (internal diameter 0.75–1.5 mm) with fine-grained packing (30–35 μm) had an efficiency equivalent to 10 000 theoretical plates per metre. In order to attain the optimum carrier gas flow rate (2.5 cm s^{-1}) in a column 1.5 m long and containing this type of sorbent, a pressure of 25 atm is necessary. It was concluded[29] that packed columns with an efficiency equivalent to 50 000 theoretical plates, which requires a length of 6 m, a pressure of 50 atm, and a volume flow rate at the outlet from the column of 5 ml min^{-1}, are realistically attainable.

Consequently there are two ways of attaining a high-efficiency of PCC: (1) by increasing the column length; (2) by employing short columns with a very fine-grained packing. We believe that the first procedure is preferable, because the use of highly efficient long PCC involves the employment of relatively low pressures at the inlet to the column. Short columns with a very fine-grained packing require an inlet pressure higher by an order of magnitude in order to achieve the same efficiency as for long PCC, which entails difficulties as regards apparatus. Furthermore, the resistance of long PCC may be appreciably reduced by employing surface-layer sorbents with large-diameter particles, since the efficiency of columns with such a sorbent is independent of particle size[55].

3. The Influence of the Nature of the Carrier Gas

According to the D'Arcy law, the pressure gradient is proportional to the viscosity of the flowing medium, so that the inlet pressure in PCC may be reduced by employing carrier gases with low viscosities. The usefulness of ammonia as the carrier gas has been demonstrated[56]. The viscosity of ammonia is a factor of 1.8 smaller than that of nitrogen and a factor of 2 less than that of helium. The density of ammonia is intermediate between those of nitrogen and helium, so that the diffusion coefficients of the components in ammonia should be higher than in nitrogen and this should lead to a higher efficiency if the spreading of the band is determined by the slow mass transfer in the mobile phase. In order to confirm these hypotheses, a study was made[56] of the dependence of column efficiency on the nature of the carrier gas. A spiral glass column 5.5 m long and with an internal diameter of 0.8 mm, filled with Chromaton N treated with 3% potassium hydroxide (160–200 μm) and impregnated with 10% Apiezon L, was used. Nitrogen, helium, and ammonia were compared as carrier gases.

Table 4. The values of H_{min} and C in packed capillary columns for different carrier gases.

Component	H_{min}, mm			10^2C, s		
	nitrogen	ammonia	helium	nitrogen	ammonia	helium
Heptane	0.82	0.85	1.0	2.0	1.5	0.8
Octane	0.65	0.70	0.84	2.4	1.7	1.2
Toluene	0.74	0.68	0.92	1.6	1.2	0.8
m-Xylene	0.66	0.63	0.82	1.7	1.4	0.9

The experimental results (Fig. 7 and Table 4) show that the employment of ammonia reduces the coefficients of resistance to mass transfer compared with chromatography in a stream of nitrogen, virtually without impairing the efficiency $H_{\min}$. Compared with helium, ammonia leads to a considerable increase of efficiency in the region of $H_{\min}$. The use of ammonia as the carrier gas in packed capillary columns is justified also because of its main advantage—a low pressure gradient. Thus, for the column used in the above investigations, with $u = 10$ cm s^{-1}, the pressure at the inlet was smaller by a factor of 1.5 compared with nitrogen (5.9 atm) when ammonia was used (3.8 atm) and smaller by a factor of 1.6 compared with helium (6.2 atm).

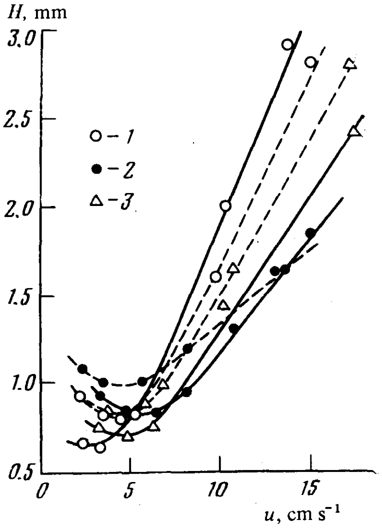

Figure 7. Dependence of H on u for different carrier gases: 1) nitrogen; 2) helium; 3) ammonia; continuous lines—octane; dashed lines—heptane.

The use of ammonia as the carrier gas to accelerate prolonged analyses has been demonstrated[56] in the separation of alkylcyclohexanols. The analysis was performed on a column 14.8 m long with an internal diameter of 0.8 mm filled with Chromosorb W containing 5% of Carbowax 20M at 160°C. Peaks of 32 compounds were detected on the chromatograms. Table 5 shows that the use of ammonia instead of nitrogen made it possible to reduce the analysis time by a factor of 1.6 without impairing the separation. For the same analysis time, a more clear-cut separation is attained and the pressure at the inlet to the column is smaller by a factor of 1.7.

The employment of ammonia as the carrier gas has the following advantages over the carrier gases usually employed (nitrogen and helium): (1) the pressure drop diminishes owing to the lower viscosity, which is important for long PCC; (2) when ammonia is used, $H_{\min}$ is smaller than in the case of helium; (3) the capacity of ammonia cylinders is larger than that of nitrogen and helium cylinders, which makes it possible to change cylinders less frequently and to employ small cylinders for mobile chromatographs; (4) the symmetry of the chromatographic bands is sometimes improved owing to the adsorption of ammonia on the active centres of the solid carrier[57].

Table 5. Results of the separation of alkylcyclohexanols using different carrier gases.

Carrier gas	P_i, atm	u, cm s^{-1}	Duration of analysis, min
Nitrogen	8.5	4.0	130
Ammonia	5.0	4.0	125
Ammonia	7.5	6.2	82

IV. THE PREPARATION AND USE OF PACKED CAPILLARY COLUMNS IN GAS CHROMATOGRAPHS

1. The Preparation of Packed Capillary Columns

Short capillary columns, (with a length up to 5 m) can be filled by hand with a sorbent prepared beforehand, either by tapping the column or by moving a mechanical vibrator down its length[58]. These procedures make it possible to obtain columns reproducible with respect to both packing density and retention characteristics. A common disadvantage is the possibility of filling with the sorbent only disassembled and short columns. The overall efficiency of short columns is low; in order to obtain highly efficient columns, it is desirable to increase their length to 10 m and more while retaining their high specific efficiency. Furthermore, the employment of these sorbents imposes a limitation on the material of the columns; for example, one cannot use glass capillaries, which have many significant advantages compared with metallic capillaries. Thus, on contact with a metallic surface, certain substances are sorbed irreversibly or decomposed[59-63]. A glass surface is chemically highly inert (the chemical inertness of glass is superior to that of diatomaceous brick). The possibility of direct observation of the filling of glass columns and of the visual changes occurring in them greatly facilitates the experiment. An important advantage of glass capillary columns is also the relatively ready availability of the apparatus[3] for the preparation of capillaries of the required length and diameter.

The methods developed recently for the preparation of long PCC, including glass ones, have extended the scope of their application in gas-chromatographic analysis. The procedure proposed by Cramers et al.[53] is as follows. A spiral tube (glass or metallic), arranged horizontally, is connected to a cylindrical container, the packing is poured into the container, and the latter is connected to the pressure supply line. The lower part of the container and almost the entire spiral tube are placed in an ultrasonic bath, the second end of the column being placed above the level of the bath. Vibration and pressure promote a continuous transfer of the packing into the column. By maintaining an approximately constant pressure drop across the filled part of the column, a homogeneous packing density throughout the column is ensured. The final pressure depends on the material of the packing employed, but it should be approximately 0.4–0.2 atm per metre of column length (the first figure refers to Chromosorb and the second to glass beads). The time required for filling is 1–2 min per metre of the column. The homogeneity of the packing particles, the scatter of which should be not more than 20 μm, is important. Dust particles are removed by vacuum screening. Depending on the density of the carrier, flotation or sedimentation may be used instead of screening to obtain a homogeneous fraction. Columns with lengths up to 15 m and internal diameters of 1.0–0.6 mm, the efficiency of which was equivalent to 3500 and 3000 theoretical plates per meter (with satisfactory reproducibility) for glass beads and Chromosorb respectively, were obtained by this method described above.

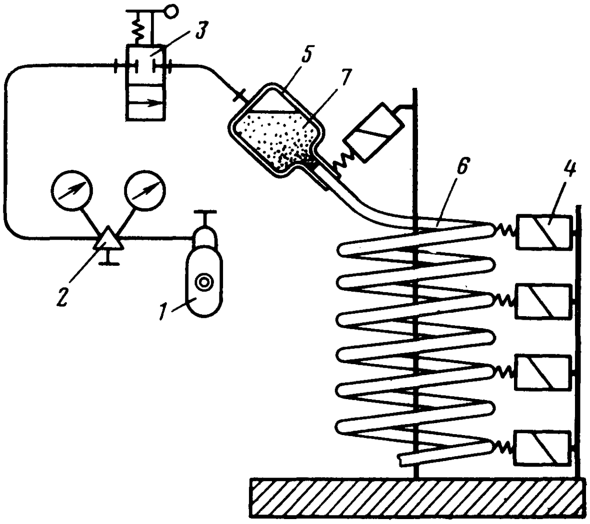

Figure 8. Schematic illustration of the device for filling capillary glass columns with the sorbent[64].

A simpler device, which does not require the use of an ultrasonic bath and is also based on the action of two factors—the vibration of the column and the pressure of an inert gas—has been developed[64]. The vibration is achieved by means of electromechanical low-frequency (50–100 Hz) vibrators placed at certain points along the length of the column. To improve the effectiveness of the stream, the pressure at the outlet from the column is applied in pulses in accordance with a specified programme†. The device (Fig. 8) consists of a compressed gas cylinder *1*, to which a valve *3*, with an electromechanical actuating device for the periodic application of pressure, is connected via a reduction valve *2*, and stands with several vibrators consisting of PE-20 electromagnetic relays *4*, with a vibration frequency of 100 Hz. A reservoir *5*, for the sorbent *7*, is attached to one of the stands, and clamps used to hold the column *6* are attached to the remaining stands. The relays are mounted along the circumference of the common base in such a way that the filled column is held by the clamps at intervals corresponding to 5–10 turns (depending on the column length).

The columns are filled as follows: a portion of the sorbent (1–2 cm^3) is poured into the reservoir *5*, the supply of gas is turned on, the automatic pressure programmer *3* is started simultaneously, and the vibrators *4* are switched on. Under the influence of the gas stream and the vibration, the sorbent is continuously transferred to the column. To ensure rapid and effective filling of the columns, the sorbent must be subjected to preliminary screening and the 100–160 and 160–200 μm fractions are used. The above device can be employed to fill spiral gas columns with various sorbents, including those which are readily charged electrically. Rapid filling by the latter is achieved by saturating an inert gas with the vapour of a polar liquid (for example ethanol); for this purpose, a porous material moistened with the liquid is placed in the reservoir with the sorbent, but does not come into contact with the latter. The device makes it possible to fill with the sorbent glass columns having lengths up to 20 m and more and with an internal diameter in the range 0.6–1.2 mm, a satisfactory reproducibility being achieved as regards both packing density and efficiency. The efficiency of the columns was equivalent to 3000 and sometimes up to 4000 theoretical plates per metre[65], which is not less than the efficiency of the columns obtained with the aid of ultrasound.

Bruner and coworkers[46,47] filled with the sorbent metallic columns having lengths up to 15 m and internal diameters in the range 0.7–0.8 mm without using a vibrator. The tube was extended in a vertical position, the lower end being fixed in such a way that the tube was subjected to a certain amount of tension. The upper end was connected to a small reservoir containing the packing, which was compacted by tapping with a rubber rod. The efficiency of the resulting columns was equivalent to 2000–2500 theoretical plates per metre of column length.

Less effective columns (1250 theoretical plates per metre) were prepared[66] by connecting individual filled sections, having lengths up to 3 m, by means of special junctions. Columns having lengths up to 12 m and an internal diameter of 1 mm were prepared.

2. Chromatographic Apparatus for Packed Capillary Columns

The use of PCC imposes a number of requirements on the apparatus owing to the following characteristic features of the analysis on such columns: low flow rates of the carrier gas, high efficiency, and high speed of analysis. In order to reduce the spreading outside the column, the volumes of the metering device, the connecting tubes, and the detector must be reduced to a minimum. Fig. 9 illustrates schematically the connection of a packed capillary column to the metering device and the detector, which makes it possible to inject the sample without dividing the stream[53]. The sample is introduced into the column via a tubular glass insert 11 cm long and with an internal diameter of 0.8 mm. One end of the insert, used to make a junction with the column, is broader and conical in shape. The column is fitted onto the cone to a depth of 2 mm. A seal is achieved with the aid of a silicone rubber washer. The exit end of the column is inserted in a stream of hydrogen and nitrogen in a flame-ionisation detector[53].

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†An effective and comparatively rapid filling can be achieved also with a continuous application of pressure.

The volume of the metering device may be reduced by employing a metallic insert with an internal diameter of 0.8–1.0 mm. Another way of reducing spreading in the metering device involves the employment of a stream divider. The stream can be divided in proportions corresponding to a small ratio (1 : 2–1 : 5), which is required merely to increase the rate of passage of the sample through the metering device.

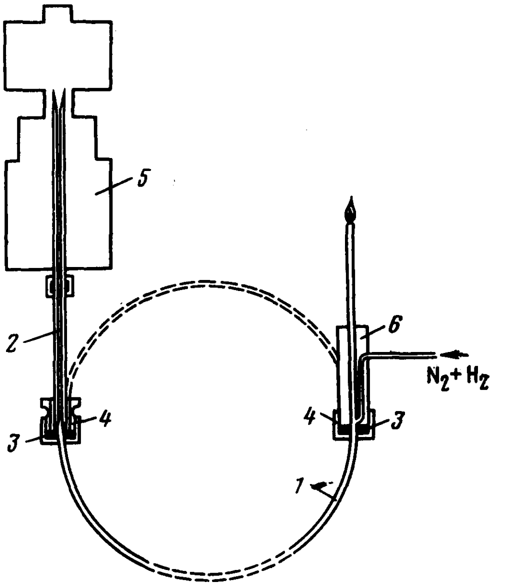

Figure 9. The connection of PCC to the gas-chromatographic system: 1) capillary column; 2) glass tube 0.8 mm in diameter; 3) silicone rubber; 4) lock-nut; 5) evaporator; 6) detector.

When PCC are used in industrial chromatographs, where samples are introduced automatically, particular attention must be devoted to the metering system. Special studies[28] on gas metering devices of membrane and plunger types in commercial chromatographs showed that, during the period of transport from the metering device to the column, the volume of the sample greatly increases and, with decrease of the initial volume of the sample, the relative increase in volume becomes more pronounced. Thus an initial sample volume of 0.15 cm^3 at a flow rate of 5 cm^3 min^{-1} increases by a factor of 8.7. To reduce the spreading, a membrane metering device, where "dead" volumes had been eliminated from the switching valves, was prepared and tested[28]. In the tests the column was replaced by a detection system, which determined the profile of the sample at the inlet to the column. The results of the test showed that, for a sample volume of 0.15 cm^3 and a carrier gas flow rate of 5 cm^3 min^{-1}, the volume of the sample increases by a factor of 5.3, i.e. is smaller by a factor of 1.5 than in a commercial metering device. A metering device of this design can be recommended for use with PCC in commercial chromatographs.

Table 6[67] presents the parameters of the sample for a metering system with switching valves. Using Klinkenberg's expression[68]

$$V_S \leqslant \frac{0.5}{N^{1/2}} V_R,$$

(where V_S is the volume of the sample at the inlet to the column, V_R the retention volume of the component, and N the number of theoretical plates) and the data in Table 6, it is possible to calculate the permissible initial volume of the sample. Thus, for a permissible sample volume of 0.8 cm^3 and a carrier gas flow rate of 0.5 litre h^{-1}, the volume of the initial sample must be not more than 0.1 cm^3.

Table 6. Parameters of the sample for a metering system incorporating switching valves without "dead" volumes.

Parameter	Carrier gas flow rate, litre h^{-1}	Volume of initial sample V_g, ml			
		0.1	0.15	0.5	1.0
Volume of sample at inlet to column, cm^3	0.1	0.55	0.6	0.75	—
	0.15	0.62	0.7	0.85	—
	0.3	0.72	0.8	1.0	1.5
	0.5	0.82	1.0	1.2	1.7
	0.8	0.92	1.15	1.4	2.0
	1.0	1.1	1.4	1.8	2.45
Ratio of given sample volume to initial volume	0.10	5.5	4.0	1.5	—
	0.15	6.2	4.7	1.7	—
	0.3	7.2	5.3	2.0	1.5
	0.5	8.2	6.7	2.4	1.7
	0.8	9.2	7.7	2.8	2.0
	1.0	11.0	9.3	3.6	2.45
Ratio of the concentrations in the sample at the maximum and in the initial sample	0.1	0.6	0.7	1.0	—
	0.15	0.55	0.65	1.0	—
	0.3	0.5	0.6	1.0	1.0
	0.5	0.42	0.45	0.9	0.95
	0.8	0.36	0.4	0.8	0.85
	1.0	0.32	0.35	0.7	0.8

The columns may be connected to the metering device in the detector either directly (Fig. 9) or via a metallic capillary. One should note that the scheme illustrated in Fig. 9 has been used in a chromatograph prepared in the laboratory. On the other hand, in commercial chromatographs such arrangement of the column is not possible and the ends of the column must be straightened before filling. This method of attachment is most effective from the standpoint of reducing the spreading outside the column and the possibility of employing columns at high temperatures (up to 260°C), but it is fairly laborious. A simpler procedure[27] involves making a connection via a metallic capillary: small sections of a metal capillary, the external diameter of which is smaller than the internal diameter of the column, are joined to the detector of the metering device (also via a silicone rubber washer). The ends of the capillaries are inserted into the inlet and outlet of the column and are glued on by means of an epoxy-resin. In this method of connection there is no need to straighten the ends of the column and the metal capillary and not the column itself is clamped by a nut, which is a much more reliable arrangement. For high-temperature analysis, it is necessary to use heat-resistant adhesives, or intermediate capillaries made of alloys (for example Kovar), forming a junction with glass, must be employed.

Flame-ionisation detectors are mainly used in conjunction with PCC. Owing to their considerable inertia, katharometers impair the quality of the separation and reduce the column efficiency. Comparative results of analyses of the products of the hydrocracking of heptane on PCC in conjunction with commercial katharometers of a polydiffusion type and with a flame-ionisation detector showed[28] that, when the latter was used, the specific efficiency of the column was equivalent to 1200 theoretical plates, while in the experiment with a katharometer the efficiency was equivalent to only 400 theoretical plates. However, the katharometer has significant advantages owing to its universality, simplicity of the apparatus involved, ease of operation, and reliability.

Studies have been made[28] on the possibility of employing a katharometer in work with PCC. The inertia of the katharometer is determined by the volume of the chamber and the inertia of the sensor elements. It has been established that the main factor determining the inertia of the katharometer is the volume of the detector chamber. A microkatharometer with a volume of the chamber of 40 μl, in which the same sensor elements as in an ordinary katharometer are employed, was therefore developed for experiments with PCC[28].

Certain requirements must also be met by the system for the recording of the results of analysis when short columns are used in rapid analysis. The limited speed of the response of the recording device is the cause of the distortion of the shape and amplitude of the chromatographic peaks, if the width of the latter is smaller than the permitted value. If the speed of the response of the recording device is T, then the minimum width σ_f of a chromatographic peak with a height h_0, which can be measured without distortion of its shape, may be determined from the relation

$$\sigma_f \geqslant \frac{h_0}{l}\frac{T}{1.65}, \tag{6}$$

where l is the length of the scale and h_0 the amplitude value of the signal. For the peak amplitude, we have correspondingly[69]

$$\sigma_a \geqslant \frac{h_0}{l}\frac{T_a}{2,22}. \tag{7}$$

The minimum permissible width of the peak at any specified height, for which the peak is measured with the specified response time of the recording device without distortion of the shape or height respectively, can also be determined from Eqns. (6) and (7). The minimum possible duration of analysis on a column with a specified efficiency can be determined from the minimum permissible peak width. The period from the instant of the injection of the sample into the column to the instant when the peak maximum emerges (t_R) is defined by the equation[28]

$$t_R = (N/5{,}54)^{1/2}\tau_{0,5}.$$

Having expressed the peak width in terms of the standard deviation σ (the peak half width at a height $h = h_{\max}e^{1/2}$), we can obtain

$$t_R = (N/5{,}54)^{1/2}\cdot\sigma\cdot 2\sqrt{2\ln 2} \simeq \sigma N^{1/2}.$$

Hence the minimum permissible elution time of the component for recording without distortion of the shape and amplitude of its peak is determined respectively by the expressions

$$t_{R_f} = \frac{h_0}{l}\frac{T}{1.65}N^{1/2}; \qquad t_{R_a} = \frac{h_0}{l}\frac{T}{2.2}N^{1/2}.$$

V. THE APPLICATIONS OF PACKED CAPILLARY COLUMNS IN GAS CHROMATOGRAPHY

1. The Separation of Complex Mixtures

The separating capacity of chromatographic columns can be increased by increasing either the sorbent selectivity or the efficiency of the columns employed. The use of selective sorbents is effective only for the separation of pairs of substances which differ in their properties; for the separation of multicomponent mixtures consisting of narrow fractions of substances whose properties differ little, highly efficient columns are necessary. The only method for the separation of multicomponent mixtures available at present is classical capillary chromatography, employed mainly for the analysis of non-polar compounds. The preparation of highly efficient capillary columns with a polar phase requires special treatment of the surface of the columns and still constitutes an art [rather than a science]. Packed columns can be filled with any sorbent and the scope of detailed studies of multicomponent mixtures of different compositions is thus extended. It is particularly useful to employ PCC for the separation of substances with small partition coefficients.

Table 7. Results of the separation of industrial mixtures of oxygen-containing compounds on capillary and ordinary packed columns.

Type of column	Sorbent	t, °C	Mixture analysed	Efficiency, N		No. of separated components
				overall	specific, per metre	
13.8 m x 0.8 mm PCC	15% PEG-400 on Chromosorb P	120	Product of oxo synthesis in Salavat [Combine]	42 000	3000	40
Ditto	ditto	120	crude alcohol	42 000	3000	46
"	"	120	ether head	42 000	3000	50
"	"	100	ditto	42 000	3000	55
"	"	140	hydroformylation product	42 000	3000	61
"	22.2% DOP + 0.5% OP-10 on celite 545	120	ditto	30 000	1700	38
4 m x 3 mm ordinary backed column	ditto	120	"	1 800	450	19
Ditto	10% PEG-2000 on INZ-600	80	"	1 773	440	14

Highly efficient PCC have been applied successfully to the determination of the compositions of complex hydrocarbon mixtures—fractions of liquid high-temperature pyrolysis products[70] and fractions (150–180° C) of the petroleums of the Surgut deposit (Western Siberia)[27]. Analysis of the C_4–C_{13} petroleum cracking fraction on PCC by gas–liquid–solid chromatography established[47] that, in terms of the number of peaks, the resulting chromatogram is analogous to that obtained on a classical capillary column.

The separation of light hydrocarbons on a usual packed column is fairly difficult. Using the main advantage of PCC—high efficiency and the possibility of filling with any sorbent—it is possible to achieve a clear-cut separation of light hydrocarbons[53].

The separation on PCC of multicomponent mixtures incorporating polar components is of particular interest. Specimens of industrial mixtures of oxygen-containing compounds—products obtained at different stages of oxo synthesis—has been studied[27] with the aid of PCC. The results of the separation are presented in Table 7, which includes for comparison also data for the separation of certain specimens on ordinary packed columns. Table 7 shows that PCC make it possible to detect on the chromatogram a number of peaks greater by a factor of 2–4 than on ordinary packed columns.

A multicomponent mixture of hydrocarbons and C_8–C_{12} alcohols, obtained as a result of synthesis from carbon monoxide and hydrogen, was separated by PCC under isothermal conditions in combination with linear programming conditions[27]. The duration of the entire analysis was 210 min; during the first 30 min, the separation was carried out at 120°C and during the next 30 min linearly programmed heating at a rate of 2 K min^{-1} was employed up to 160°C, this being followed by isothermal conditions. The chromatogram presented in Fig. 10 shows that under these conditions a fairly clear-cut separation of 60 components is achieved, and that during linearly programmed heating there is almost no displacement of the base line.

The advantages of PCC in the separation of polar compounds have been demonstrated[71] in the analysis of C_1–C_6 alcohols, aliphatic acids, and primary amines. Highly efficient PCC have also been used to analyse complex mixtures of steroids[53], barbiturates[54], organic mixtures in water[47], and impurities contaminating air[46,47] and for the separation of the stereo-isomers of acyclic hydrocarbons[72] and structural isomers of aromatic hydrocarbons[72].

2. Analysis of Impurities

In the determination of impurities it is necessary (1) to separate them from the main component and then from one another, and (2) to carry out the determination under optimum conditions as regards sensitivity, i.e. under the conditions of maximum concentration in the centre of the zone. In order to separate the impurities from the main component, a much higher column efficiency is necessary than in the separation of zones with identical concentrations. Thus, in the separation of substances with a concentration ratio of 1000, it is necessary to employ a column with an efficiency higher by a factor of 2.8 than that of the column used to separate substances with identical concentrations[74].

In conformity with the theoretical plate theory[75,76], the maximum concentration in the zone increases with efficiency and with the weight of the sample:

$$C_{\max} = \frac{N^{1/2}}{V_R}\,\frac{q}{(2\pi)^{1/2}},$$

where q is the weight of the sample.

The simplest method of increasing the sensitivity is to increase q. However, an increase of q entails a decrease of column efficiency and an impairment of separation. For this reason, it is in many cases more useful to employ highly efficient columns.

The capillary columns proposed by Golay[1] have been and still are the most efficient chromatographic columns. However, owing to their disadvantages they have not found applications on quite such a wide scale as packed columns. In particular, one of the disadvantages of classical capillary columns is the difficulty and in many instances the

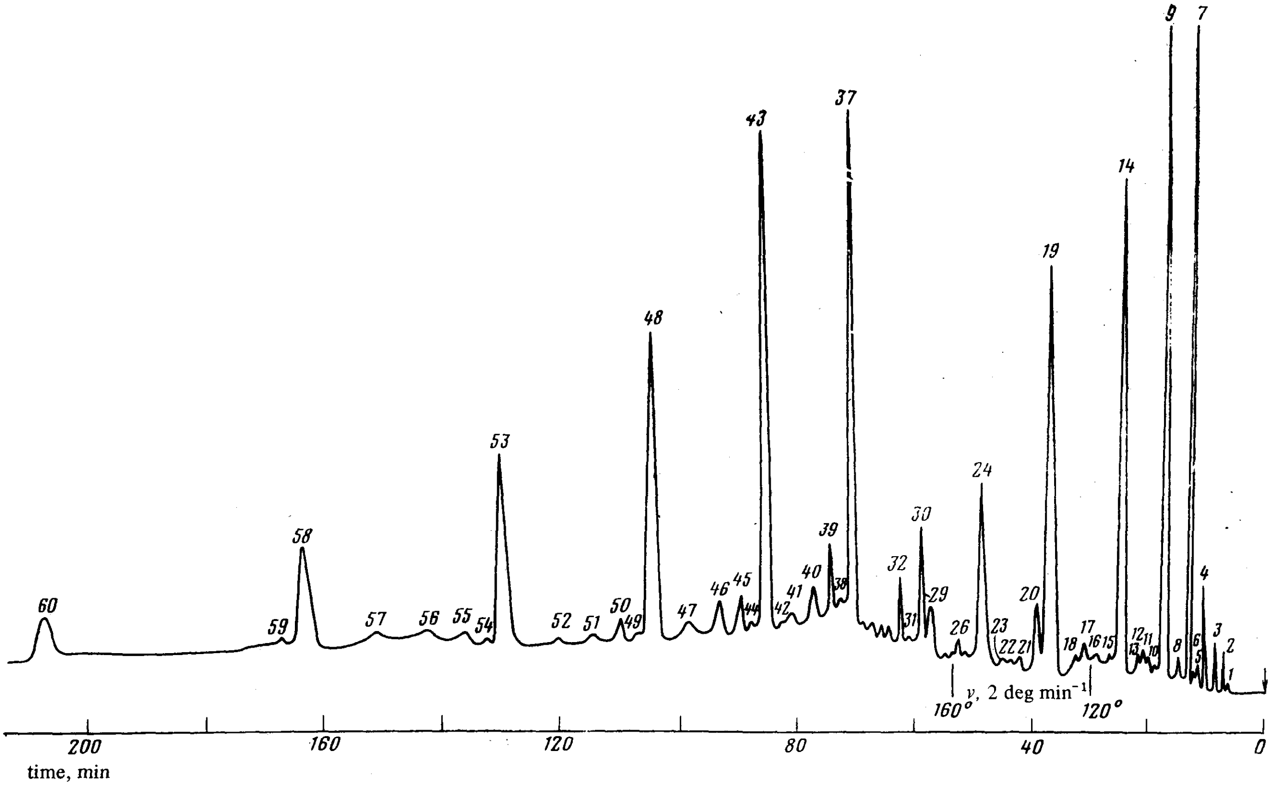

Figure 10. Chromatogram of the separation of the oxo synthesis products. 15.5 m × 0.8 mm column; sorbent—15% of 1,2,3-tris-(2-cyanoethoxy)propane on Chromosorb P.

impossibility of analysing admixtures and especially microimpurities, since, owing to the extremely small amount of charge which the columns can handle, the determination of impurities requires unduly sensitive detecting systems. Furthermore, the high phase ratio β impairs the separation, which has a particularly marked effect in the separation of weakly sorbed compounds. These disadvantages may be to a large extent eliminated by employing long PCC, the small diameter of which ensures their high efficiency, and the presence of a sorbent ensures a high capacity.

If H is increased by 10% compared with the limiting value H_c for an infinitesimally small sample, then the limiting sample size V_{lim} can be estimated from the equation[77]

$$V_{lim} \simeq 0.2 V_R / N^{1/2},$$

or, assuming that $V_R \simeq K v_l$ (K is the gas–liquid partition coefficient and v_l the volume of the SLP in the column), from the expression

$$V_{lim} \simeq 0.2 K v_l / N^{1/2}.$$

In comparing the limiting sample sizes for capillary (V^c_{lim}) and packed capillary (V^{cp}_{lim}) columns, it is useful to employ the relation

$$V^{cp}_{lim} / V^c_{lim} = v_l^{ce} / v_l^c, \tag{8}$$

where v_l^{cp} and v_l^c are the volumes of SLP in packed capillary and classical capillary columns respectively. Eqn. (8) was obtained on the assumption that the number of theoretical plates in the columns compared and the partition coefficients in the latter are similar. Since the volume of the SLP in PCC is approximately 100 times greater (see Section II) than in classical capillary columns, the sample size in PCC is one hundred times greater than in classical capillary columns. Consequently, when detectors of the same sensitivity are used, the minimum concentration of the impurity which can be determined with the aid of PCC is approximately 100 times smaller than that which can be determined by means of classical capillary columns.

Additional advantages of PCC compared with classical capillary columns are the possibility of employing mixed sorbents and the possibility of gas–adsorption chromatography in packed capillary columns.

Long PCC have been used[78] to determine impurities in 2-bromo-2-chloro-1,1,1-trifluoroethane (fluorothane). The separation of the isomeric 1-bromo-2-chloro-1,1,2-trifluoroethane impurity from the main substance constitutes a particular difficulty in this analysis. The application of PCC in the analysis of fluorothane made it possible to determine a larger number of microimpurities (almost by a factor of two). Furthermore, this ensures a higher separation factor ($R \gg 1$) for the main component and the isomer[78,79].

The use of short PCC permits the determination of microimpurities by a micromethod[13] and a high-speed method[19]. The authors of these investigations carried out an analysis (at 70° C over a period of 70 min) of microimpurities in isoprene on a 2.5 m × 1.1 mm column filled with modified (with 2% of squalane) alumina; H for 2-methylbut-1-ene amounted to 0.04 cm. Rapid analysis of the same isoprene specimen (at 30° C over a period of 7 min) was carried out on a 0.5 m × 0.6 mm column with the same adsorbent; in this case H for the same component was 0.06 cm. Fig. 11 shows that the reduction of the analysis time by a factor of 10 is entirely worthwhile, despite the slight impairment of efficiency. One should also note that rapid analysis has been achieved for a much lower temperature, which is very important in experiments with readily polymerisable substances. The content of the impurities determined in the two instances was 2 × 10^{-4} vol.%.

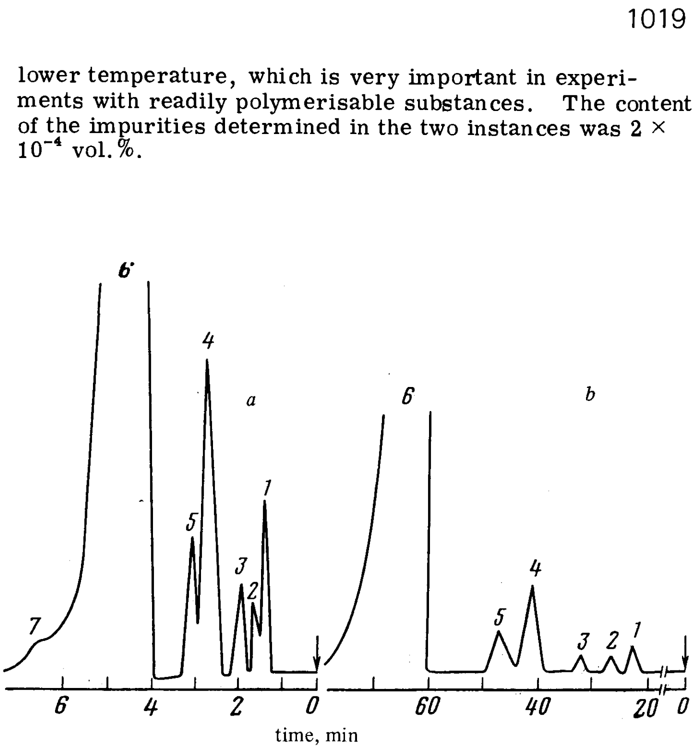

Figure 11. Chromatograms of the separation of impurities in isoprene: *a*) high-speed method; carrier gas (hydrogen) flow rate 50 cm s^{-1}; 30° C; *b*) usual analysis; carrier gas (nitrogen) flow rate 8.1 cm s^{-1}; 70° C; 1) 3-methylbut-1-ene; 2) pent-1-ene; 3) pent-2-ene; 4) 2-methylbut-1-ene; 5) 2-methylbut-2-ene; 6) isoprene; 7) butadiene.

Packed capillary columns have been used[31] to determine gaseous hydrocarbon impurities in the propane–propene fraction used to make polypropylene. The high-speed method for the determination of microimpurities has been applied in gas-adsorption chromatography on alumina modified with 3% of squalane using a programmed temperature up to 70° C. The analysis time of an artificial propane–propene fraction consisting of 13 components was 8–10 min (on a column of the usual type, it is 40 min); the volume of the sample injected was 2 cm^3. The column efficiency H for α-butene was 0.028 cm, i.e. was close to H for classical capillary columns. The minimum impurity content in the sample was 8 × 10^{-4} vol.%.

3. High Speed Analysis

When a gas chromatograph is used as a pulse generator for the regulation of chemical processes, the duration of the analytical cycle must be reduced, i.e. high speed analysis is necessary. It is also required in routine analyses, in the study of complex multicomponent systems, in kinetic measurements, etc. The duration of analysis may be reduced by means of a higher separating capacity of the column under optimum separation conditions, by increasing the flow rate at the mobile phase, and by employing shorter columns, high-speed amplifiers, and computer integrators.

Since PCC are characterised by high resolving capacity per unit length, this makes it possible to employ short separating systems. The high permeability of columns of this type permits the use of higher carrier gas flow rates, which can be ensured by moderate pressures. The stable conditions which obtain when the temperature is programmed permit an increased rate of separation by programming the temperature and pressure without an appreciable decrease of separating capacity.

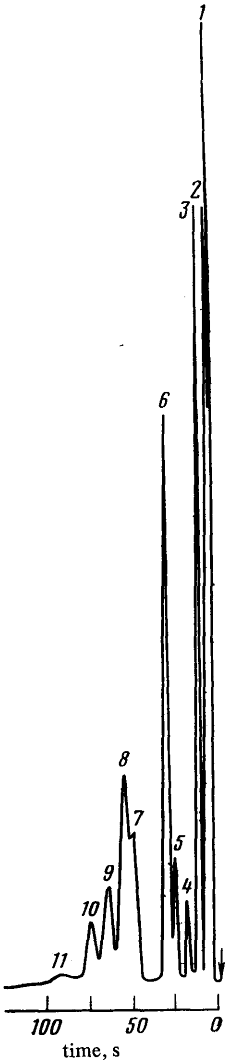

Figure 12. Chromatogram of the high-speed separation of C_1-C_4 hydrocarbons. 0.2 m × 0.58 mm column; carrier gas (hydrogen) flow rate 40 cm min^{-1}; room temperature: 1) methane; 2) ethylene; 3) propane; 4) n-butane.

Kaiser[80] suggested that the carrier gas pressure and the separation number per unit time Tz/t be used as the principal characteristics of high-speed chromatographic separation. The separation number Tz is defined by the relation

$$Tz = \frac{t_2 - t_1}{\tau_{0.5}^{(2)} + \tau_{0.5}^{(1)}} - 1,$$

where t_1 and t_2 are the uncorrected retention times of the first and second components and $\tau_{0.5}^{(2)}$ and $\tau_{0.5}^{(1)}$ are the widths of peaks at the level of half their height. The separation number can be measured with programmed temperature and pressure, so that it is preferable as a criterion to measurements based on the theoretical plate theory. Short PCC have been assessed[80] in terms of the proposed criteria when the columns were used for high-speed analyses.

Capillary columns filled with a sorbent have been employed[31] for the high-speed analysis of low-boiling C_1-C_4 hydrocarbons by gas-adsorption chromatography on modified alumina. A mixture of eleven components was separated in 90 s. An example of high-speed analysis of a mixture of light hydrocarbons over a period of 3.5 s is illustrated in Fig. 12 (column with alumina gel modified with the aid of 5% of squalane). The methane elution time was less than 1 s and the column efficiency for n-butane was $H \simeq 0.1$ cm.[31]

A further decrease of the duration of analysis is hindered by difficulties associated with the apparatus. Thus the sample injection time is almost equal to the elution time of the first component, which distorts the shape of the peak; it is impossible to measure accurately the elution times of the components with the aid of the usual stop watch (the error of the measurement is 100% and more); the unduly high volume flow rates in a flow-type detector limit stable combustion and accuracy of the measurement. High-speed analysis (1 peak in 1 s) therefore requires special automatic metering, recording, and integrating (counting) devices.

The possibility of reducing the duration of analysis by a factor of 2-5 has been demonstrated[81] in a study where capillary columns filled with Spherosil were used in gas-solid chromatography and gas-solid chromatography with a modified SLP.

4. The Use of Packed Capillary Columns in Industrial Automatic Chromatographs

Industrial automatic chromatographs are used as sensors of composition in automatic monitoring and control systems for technological processes. A specific feature of industrial chromatographs is that they are mounted directly at the sampling points in technological apparatus and operate under automatic conditions. These devices must therefore be more compact, must require a fairly small amount of carrier gas, and must be reliable. The columns in such apparatus must meet another requirement: long operating time without alteration of the characteristics of the separation process. For this reason, the number of sorbents and liquid phases suitable for industrial chromatographs is much smaller than for laboratory chromatographs. Apart from characteristics such as sensitivity and error, an important parameter of industrial chromatographs is the analysis time, which determines the possibility of obtaining information about the composition of the mixture analysed in a specified time.

Packed capillary columns satisfy all the requirements enumerated above to a much greater extent than the usual packed columns. The high specific efficiency of PCC and the possibility of carrying out analyses at a fairly high linear flow rate of the carrier gas without reducing the efficiency of the separation make it possible to reduce greatly the duration of the analysis. The small amounts of carrier gas and sorbent required permit the use of scarce and expensive carrier gases and sorbents and the small size of the columns permits the construction of a compact analyser ensuring effective temperature control and the possibility of ensuring any category of protection from explosion.

However, one should bear in mind that PCC impose definite requirements, primarily as regards the automatic metering device and the detector. Thus, when appreciable spreading of the sample occurs in the metering system, the column is overloaded, and its efficiency falls[66]. The inertia of the detector should correspond to the parameters of the peak[82], otherwise the apparent efficiency of the separation falls, and an appreciable error is introduced into the results of the measurements.

The following apparatus has been developed[81]: an automatic metering device and a low-inertia thermal conductivity detector, suitable for PCC, and on their basis, an industrial automatic "Mikrokhrom" chromatograph with an explosion-resistant device was constructed. The apparatus has been used successfully for the determination of the compositions of many industrial mixtures directly in industrial plants.

In the study of individual stages of the technological processes under development automated pilot microapparatus has been used recently. One of the most important parameters in the assessment of the results is the composition of the multicomponent mixture at the outlet from the microreactor. The most suitable analyser is a compact high-speed automatic chromatograph with a small volume of samples removed (this makes it possible to calculate the material balance without taking into account the amount of substance taken for analysis). The chromatograph with PCC meets the above requirements to the greatest extent.

The Mikrokhrom chromatograph of normal design (not the explosion-resistant design) has been used in experiments with a pilot microapparatus for catalytic hydrocracking[83]. The chromatogram of a mixture of catalytic n-heptane hydrocracking products is illustrated in Fig. 13.

5. Measurement of Physicochemical Characteristics

One of the most important applications of PCC involves the determination of physicochemical characteristics by a micromethod, i.e. using small amounts of the test substances and the sorbent (reagent). The determination of rate constants on PCC was first developed[24] for the reaction of isoprene with maleic anhydride in the liquid phase by a chromatographic pulse micromethod. The degree of conversion was determined from the change in the area under the chromatographic isoprene peaks (n-pentane was used as the internal standard). The contact times of the reactants were calculated from the retention times of the diene taking into account the "dead" time of the chromatograph. The reaction rate constants, determined at 42°, 48°, 56°, and 62°C, and the activation energy of 12.1 kcal mole^{-1} agree satisfactorily with the values obtained on a column of the usual type[84].

An advantage of PCC is the possibility of employing them (by virtue of their high efficiency) for the determination of the rate constants for rapid reactions. A special calculation showed[24] that the kinetic coefficient of sorption and desorption (internal-diffusion mass exchange) corresponding to the maximum degree of conversion is a factor of 2×10^3 greater than the rate constant (for an analytical column, the ratio is smaller by an order of magnitude). PCC can also be used to determine heats of adsorption. The heats of adsorption of α-butene on various alumina specimens have been determined[24] using a 0.5 m × 0.58 mm PCC in the temperature range from −20° to +100°C. According to literature data[85], the heat of adsorption of n-butane is 8.2 kcal mole^{-1}; values in the range 8.5–8.1 kcal mole^{-1} have been obtained on PCC. Consequently the micromethod described above for the determination of heats of adsorption is entirely reliable and accurate.

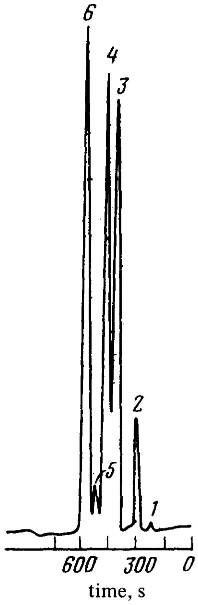

Figure 13. Chromatogram of the separation of the products of the catalytic hydrocracking of heptane. 1.2 m × 1.0 mm metallic column; sorbent—Chromosorb P (120–150 μm) impregnated with 15% of squalane; 60°C; carrier gas (nitrogen) flow rate 2.4 cm^3 min^{-1}: 1) n-hexane; 2) methylcyclopentane; 3) 2-methylhexane; 4) 3-methylhexane; 5) 3-ethylpentane; 6) n-heptane.

In conclusion we may note that PCC extend the scope of gas-chromatographic studies both in the field of analysis, particularly of multicomponent mixtures and mixtures difficult to separate, and in the measurement of physicochemical quantities. Also promising is the application of PCC in microchemistry, particularly for microseparations on a preparative scale.

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Theory of Chemical Reactivity

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This critical review deals with the present state of the theory of chemical reactivity, based on the methods of quantum chemistry and statistical thermodynamics. Reactions in the gaseous phase and in solution are examined. The static and dynamic theories of reaction rates are analysed. Catalytic reactions are discussed briefly. The bibliography contains 272 references.

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I. INTRODUCTION

The calculation of equilibrium constants and rates, based on the methods of quantum chemistry and statistical thermodynamics, is one of the most important problems of theoretical chemistry and hence is of considerable significance not only for the development of chemistry but also for its various practical applications.

For the solution of many problems in experimental chemistry it is sufficient to know the relative values of the equilibrium constants and rates in series of structurally related compounds. Nevertheless, the absolute values of these quantities for reactions taking place under different conditions is of considerable interest for present-day theoretical chemistry. Although this problem has already been solved in principle for some time, considerable difficulties are encountered in applying the theory to specific problems. In the theory of reactivity there are many problems, the solution of which requires new ideas. These ideas need not always be completely new; in some cases, the modification of old methods may lead to considerable progress. An example is provided by collision theory (in chemical reactions), the development of which has led in the last 15 years to the formulation of the present dynamic theory of reactivity.

The elementary quantum-chemical theory of reactivity, which reduced chiefly to the construction of correlations for experimental data, reached its greatest development in the nineteen-fifties [1-8] and was for the most part complete by the nineteen-sixties [4]. Even now, however, this theory is useful for chemists. In the nineteen-seventies, the development of the static theory of reactivity is taking place in the following directions [9]: a) calculations of the absolute values of equilibrium constants and rates; b) the study of the structure of the potential energy surfaces of reacting species; and c) calculations of solvation energies (this last is extremely important, since 95% of chemical reactions take place in solution).

In the second half of the nineteen-sixties, considerable efforts were directed to the study and development of the principle of the conservation of orbital symmetry,[9] which met with considerable response in organic and then inorganic chemistry. In this field, important results were obtained, which made it possible to estimate qualitatively the relative values of activation barriers and hence the possibility of a given type of reaction.

In the first part of the present review, problems at present common to the entire theory of chemical reactivity are discussed. In the second part, various theoretical studies in the field of reactivity are examined, An attempt has been made to cover completely work on the calculation of the absolute values of equilibrium constants or rates. Very little work of this kind has been published up to the present. Since the present review emphasises quantitative work, almost no attention is paid to methods for the qualitative study of reaction kinetics, except for adiabatic reactions taking place in the electronic ground state. Most attention is paid to the theory of the equilibrium and kinetics of reactions, and to various types of reaction between reagents. Some catalytic reactions are also included in the review.

II. GENERAL PROBLEMS OF THE THEORY OF CHEMICAL REACTIVITY

1. Stationary Points of Potential Energy Surfaces

Points on the potential energy surface at which the first derivatives with respect to the coordinates of all the atoms are equal to zero are called stationary points [10]. Stationary points are of particular importance in the theory of chemical reactivity. For the subsequent treatment it is convenient to divide these into three groups, on the basis of the properties of the matrix of the second derivatives of the energy with respect to the coordinates, that is the matrix of force constants. If all the eigenvalues of this matrix are positive, the point is a local minimum and corresponds to a stable conformation of the molecule. If only one eigenvalue of the force constant matrix is negative, the point is called a saddle point and corresponds to an activated complex in the sense of the theory of absolute reaction rates (see Part III). If more than one eigenvalue of the force constant matrix is negative, the corresponding stationary point is of no interest for the theory of chemical reactivity. For the description of equilibria it is necessary to consider only points of the first type, and for the description of the kinetics of processes, the points of the first and second types should be known. The determination of these points until recently presented considerable difficulties, which in practice could not be overcome for molecules containing five or more atoms.

The development of computer techniques and optimisation methods in recent years has led to the development of new algorithms for finding local minima. The method of successive optimisation of the coordinates [10], which has a low efficiency, has been replaced by more effective methods [11-25]. The rate of convergence of the calculation depends on the energy characteristics used to define the stationary points. Methods based only on energy values, in particular the simplex method [14,15], require considerable machine time; on the other hand, methods based on the use of second derivatives (of the energy with respect to the coordinates) also have a low efficiency, since the values of the second derivatives are calculated numerically from the values of the first derivatives, and this increases considerably the time required for the calculations [11-13,20,26].

The most effective methods are those which use only the first derivatives of the energy. The simplest of these, the linearly converging method of steepest descent, is less effective [20] than the quadratically converging methods of variable metrics. The Fletcher–Powell algorithm [27] has been used by Bloemer and Bruner [21], and this algorithm and those of Broyden [28], Goldfarb [29], and Hoshino [30] have been used by Pancíř [26]. The most effective method has been found to be that of Murtagh and Sargent [31], used by a number of authors [16,19,23,26]. By carrying out the optimisation of the geometry and the SCF procedure in a single iteration cycle in the CNDO/2, INDO, and MINDO/2 approximations, the time required for complete optimisation of the geometry has been decreased considerably [19].

In all cases, the determination of the stationary points of the potential energy surface is based on some initial approximation. The choice of this approximation presents no difficulty for finding local minima, since in this case the information on the structure of the molecule is usually sufficient. In the case of saddle points, the situation is more complicated (see Part III for the method for finding these points). Moreover, in the determination of saddle points it is impossible in the general case to employ methods based on the use of only the values of the energy or its first derivatives. Gardient methods are applicable only for symmetrical molecules, and then only when the eigenvector belonging to the negative eigenvalue satisfies definite symmetry conditions [16]. The calculation of the matrix of the second derivatives of the energy, which complicates the determination of stationary points, is necessary in the case of saddle points: the analysis of the eigenvalues of the force constant matrix is the only method for determining the type of stationary point, and in addition the eigenvectors give information on the direction of the reaction coordinate (see Refs. 26 and 32 for more details). Unfortunately, the time required for the optimisation of the geometry when the force constant matrix obtained by semi-empirical methods of the CNDO type are used is more than ten times the time required for the solution of this problem by the method of variable metrics [26].

2. Energy in the Hartree–Fock Method and Exact (Non-relativistic) Energy: the Problem of Allowing for Correlation Energy

Most quantum-chemical calculations are carried out in the SCF approximation. It is therefore important to know the extent to which SCF methods are suitable for the study of chemical reactivity. For this purpose, qualitative results obtained in this field, chiefly by non-empirical methods, are examined below.

One unsatisfactory feature of the SCF method is that the probability density (the combined distribution of the coordinates) of two electrons in this approximation is equal to the product of one-electron functions. This means that the motion of the electrons is regarded as taking place independently, so that no allowance is made for electron correlation. The difference between the energy obtained by exact solution and the energy from the SCF solution is called the correlation energy. The energy of the exact solution is understood to be the lowest non-relativistic energy in the Born–Oppenheimer approximation, and the energy of the SCF solution the lowest energy possible within the framework of the SCF method.

From the viewpoint of chemical reactivity, the chief disadvantage of the SCF approximation is the incorrect description of a large part of the dissociation region of the system. A classical example is the potential energy curve for the hydrogen molecule (Fig. 1). In this case it is possible to describe the dissociation correctly[33] if allowance is made for the interaction of the ground state with the doubly excited state $(1\sigma_u)^2$. In the case of the molecules C_2 and N_2, however, the correct description of the dissociation requires the use of four or ten configurations[34] respectively. Thus the solution of a problem of this type must be carried out by the method of configuration interaction or some other method taking account of correlation energy. The same unsatisfactory features of the SCF method appear in the study of activated complexes.

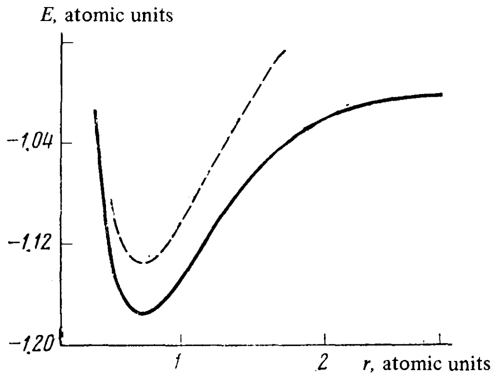
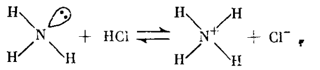


Figure 1. Potential energy curves[33] (in atomic units) for the H_2 molecule. Continuous line—exact solution, broken line—SCF approximation.

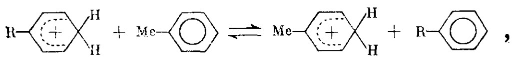
In the general case, the use of the SCF approximation to construct energy surfaces with "chemical accuracy" is fairly limited. For one type of reaction, however, the SCF approximation is satisfactory[35]. These are exothermic reactions, which, according to Polanyi[36], correspond to a potential energy surface without any barriers or activation energy. The problem of the activated complex thus diappears in this case. Moreover, for ion–molecular reactions of the type $Li^+ + H_2 \rightarrow H^+ + LiH$ the structure of the potential energy surface is determined chiefly by ion–quadrupole and ion–induced dipole interactions, which can readily be taken into account in the SCF approximation[37].

In the case of chemical equilibria, it is possible to limit the treatment to the study of fairly small regions around the minima of the energy surfaces. It has been established empirically[38,39] that the enthalpy of a reaction depends little on the correlation energy if all the reagents are systems with closed electron levels. The enthalpies of reactions, however, are not determined with an accuracy which would make it possible to carry out reliable statistical-thermodynamic calculations of the equilibrium constants. For the correlation energy to be preserved in a reaction, certain conditions must be fulfilled[40], namely: a) the number of electron pairs† should not change, and b) the relative arrangement of neighbouring electron pairs should also be preserved approximately‡.

In reactions involving molecules with filled orbitals, the first condition is often satisfied, but the second less frequently. In other words, for the preservation of correlation energy, not only in-pair interactions (in-pair correlation energy), but also between-pair interactions (between-pair correlation energy), are important. An elementary example of a reaction in which both of these conditions are fulfilled is the following[42]:

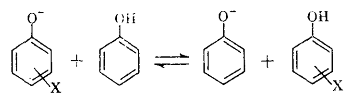

(1)

Preservation of correlation energy is also to be expected in so-called isodesmic reactions. This term was introduced by Pople and coworkers[43] for reactions in which the number of bonds of a definite formal type is preserved, but the relative arrangement of the bonds is changed. Condition (a) is always fulfilled for these reactions. Condition (b) may be fulfilled to different extents; for example, it is fulfilled to a sufficient extent in the following cases[44,45]:


(2)

$$RO^- + MeOH \rightleftharpoons MeO^- + ROH\ , \tag{3}$$

$$RCC^- + HCCH \rightleftharpoons HCC^- + RCCH\ , \tag{4}$$


(5)

The enthalpy of a reaction can often be determined indirectly; for example, for the reaction

$$NaCl \rightarrow Na + Cl \tag{6}$$

none of the above conditions is fulfilled, Since NaCl is an ionic compound, however, it is possible in the SCF approximation to study the process

$$(Na^+Cl^-) \rightarrow Na^+ + Cl^-, \tag{7}$$

---

†To keep the subsequent discussion simple, an exact definition of electron pair will not be given.

‡For example, for internal rotation in ethane. In this case the potential energy curves obtained by the SCF and PC methods are very similar[41].

for which both conditions are fulfilled, Since the correlation energies of Na, Cl, and $Na^+ + Cl^-$ are well known, this method[46] can be used to find the exact value of the enthalpy of reaction (6). Thermochemical cycles are used similarly to study so-called bond separation reactions[43]. These are isodesmic processes of the type

$$X{-}Y{-}Z + Y \rightarrow X{-}Y + Z{-}Y, \tag{8}$$

or, for example,

$$CH_3CHO + CH_4 \rightarrow C_2H_6 + H_2CO, \tag{9}$$

which are not of interest in themselves, but which can be used to obtain useful results.

A description of methods for the direct calculation of correlation energy is beyond the scope of the present review. Only a few brief points will therefore be made. Mention may be made first of the simplest method[47], in which a constant empirical value of the correlation energy is associated with each bond, and the total correlation energy is calculated as the sum of the individual contributions (just as dipole moments, heats of formation, etc. are estimated empirically in chemistry). This method can hardly give sufficiently accurate values of the correlation energy, since it does not take account of in-pair interaction. Of semi-empirical methods, mention may be made of that based on the many-electron theory of Sinanoğlu[50], in which allowance is made for the effective paired correlation energy (the EPCE method[48,49]), and the method proposed by Lie and Clementi[51], in which Wigner's equation[52] is used. The results which have been published do not yet make it possible to discuss the possibilities of these methods more fully. The results obtained by the present authors[53] for the complex $(H_2)_2$ show that the EPCE method may give useful information for the description of van der Waals interaction. An advantage of both of the above methods is their relative simplicity, but an unsatisfactory feature is the incorrect description of the dissociation limits in most cases.

Many versions of non-empirical methods exist. In some of these, however, allowance is made only for in-pair correlation energy (calculations based on the theory of geminals), or else the part played by correlation energy is overestimated, and it is usually difficult to estimate the error (the approximation of independent electron pairs, IEP [40]); other methods require a large expenditure of machine time (PC SCF methods) with allowance for a large number of configurations. A modified IEP approximation[54,55] or simple versions of the configuration interaction method[56,57] are therefore usually employed.

To conclude this section, brief mention may be made of semi-empirical SCF calculations of the CNDO and INDO types. Among those who use these methods, there is the widespread opinion that correlation effects can be taken into account by empirical parameters, so that there is no need to consider the estimation of the correlation energy. In fact, the empirical parameters are chosen in such a way that the bond energy of the molecule is reproduced for the equilibrium geometry. These semi-empirical methods, however, are based on non-empirical versions of the SCF method and therefore should exhibit all the weaknesses of this approximation, for example the incorrect description of the dissociation limits. It may be assumed, however, that the study of energy surfaces by semi-empirical methods is meaningful and that studies in this field are required, since these surfaces may give at least useful "semi-quantitative" information.

3. Calculation of Thermodynamic Functions in Statistical Thermodynamics

The quantitative estimation of the equilibrium constants and rates of chemical reactions is based on statistical thermodynamics. For the great majority of processes taking place in the gaseous phase at temperatures not exceeding 1000 K, involving normal molecules, radicals, or ions (in contrast to van der Waals complexes), the equilibrium constants (or rates) are determined chiefly by the value of ΔH_0° (or $\Delta H_0^{\neq}$). The calculation of the enthalpy change is of course a quantum-chemical problem. Thus the problem of improving the rigid rotator–harmonic oscillator (RR–HO) approximation is not the primary problem, although from the physical viewpoint it is a crude approximation. Thus the principal and very difficult problem is the calculation of the enthalpy changes by the methods of quantum chemistry. The value obtained corresponds to 0 K and does not take account of zero-point vibrational energy.

The calculation of the vibrational partition function (since it is desired to avoid the use of experimental data) can be carried out by the methods developed by Wilson and coworkers[58] and El'yashevich[59]; the zero-point energy is of course again determined. The complete partition functions can be used to calculate the values of the thermodynamic functions at any temperature. The relationships between the thermodynamic functions and the partition functions, and methods for calculating the partition functions from spectroscopic data, has been described in textbooks and monographs[60-63]. In the general case, an appreciable contribution to the total partition function is made by the translational, rotational, and in a number of cases vibrational partition functions. Analysis of the structure of the vibrational partition function shows that with increase in the temperature and decrease in the frequency of the normal vibrations, the magnitude of the contribution from the vibrational partition function increases. At temperatures not exceeding 1000 K, for systems in which there are no vibrational modes having frequencies (wavenumbers) smaller than 100 cm^{-1}, the contribution of the vibrational partition function is small. This is a favourable feature, since the purely theoretical calculation of the fequencies of the normal vibrations not only is tedious and requires considerable skill, but also is accompanied by extremely large errors.

Analysis of the literature shows that if the experimental values of ΔH_0° are used, the calculation based on the spectroscopic data and the partition functions in the rigid rotator–harmonic oscillator approximation leads to extremely reliable equilibrium constants; the error often does not exceed ±10%. The results of calculations for 33 reactions in the gaseous phase and for reactions between solids and gases have been published[64]. The error in the determination of $\lg K_p$ using the results of theoretical calculations of partition functions based on semi-empirical methods (CNDO/2, INDO, MINDO/2) has been studied[65,66]. The error introduced by the rotational partition function is independent of temperature, whereas the error due to the vibrational partition function increases with increase in temperature (by 2–3 orders of magnitude on going from 100 K to 2000 K).

In the general case, the results of the most reliable recent calculations of ΔH_0° (or $\Delta H_0^{\neq}$) indicate that the calculated values of the rotational and vibrational partition functions (based on semi-empirical quantum-chemical methods) are satisfactory. Nevertheless, it is appropriate to discuss the possibilities provided by various approximations which represent improvements on the RR–HO approximation[67].

Statistical thermodynamics provides general equations for calculating partition functions in the non-rigid rotator–anharmonic oscillator NR–ANO approximation[68]. The rotational–vibrational spectra have been studied to the extent required for the NR–ANO approximation for only a small number of molecules, however. Nevertheless, for this group of molecules it is possible to reach definite conclusions regarding the relationships between the thermodynamic functions calculated in the two approximations. For example, for the entropy of water at 1000 K, Godnev[69] gives the following data: RR–HO approximation, S^0_{1000} = 55.52 cal.mole^{-1} K^{-1}; NR–ANO approximation, S^0_{1000} = 55.598 cal. mole^{-1} K^{-1}. The calculations show that allowance for the anharmonicity and non-rigidity of the molecule introduces small corrections to the value of the logarithm of the equilibrium constant[65,70].

At the present time, for most molecules, calculations of the thermodynamic functions based on experimental data or on the methods of quantum chemistry are possible in practice only in the RR–HO approximation. Comparison of the results of calculations carried out in the RR–HO and NR–ANO approximations show that the RR–HO approximation is fully applicable, at least for rigid molecules.

It would be extremely attractive to be able to determine the molecular data appearing in the partition functions from an analysis of the potential energy surfaces. It is not very simple, however, to use the results of quantum-chemical calculations to solve problems in molecular spectroscopy. For the construction of the rotational–vibrational Hamiltonian it would be most convenient to have an analytical expression describing the potential energy surface. Even if this problem were solved, however, it is impossible to find a general analytical solution of the corresponding eigenvalue problem, and this makes the exact calculation of the partition functions impossible. With the exception of the simplest systems, energy surfaces at present cannot be represented in analytical form.

The methods of quantum chemistry can be used to find the first derivatives of the total energy, and this makes it possible to carry out the approximate calculation of the second derivatives at the stationary points (see Part II). If however it is desired to take account, albeit partly, of anharmonicity and rotational–vibrational interaction in the calculation of the thermodynamic functions, it is necessary for this purpose to find the values of the derivatives of third and fourth orders. Except for the case of diatomic molecules, the possibilities provided by present-day quantum chemistry for the solution of this problem are extremely limited[67]. At least a partial solution to this problem was proposed by Simons and coworkers[71], who introduced a new type of anharmonic potential. The results obtained up to the present indicate that it is possible to take account of anharmonicity and non-rigidity without complicating appreciably the quantum-chemical calculations, compared with the harmonic approximation.

In conclusion it may be noted again that the errors introduced into the equilibrium constant K_p in the calculation of the entropy term in the RR–HO approximation are at present much smaller than the errors in the calculation of ΔH°_0. It is therefore necessary to pay particular attention to the development of reliable methods for estimating the enthalpy term.

III. EQUILIBRIUM AND KINETICS OF REACTIONS

1. Classification of Chemical Reactions

Not only from a formal viewpoint, but also from physical considerations, it is convenient to divide reacting systems into two groups: equilibrium and kinetic. A more detailed classification of chemical processes can be carried out according to the states of aggregation of the reactants and reaction products. There are three types of homogeneous processes: reactions in the gaseous (1), liquid (2), and solid (3) phases. In addition, reactions may be heterogeneous, that is they may take place at the interface between two phases: liquid and gas (4), liquid and solid (5), and gas and solid (6).

The subsequent treatment deals chiefly with homogeneous reactions taking place in the gaseous and liquid phases, and processes of the fourth and sixth types are discussed briefly.

2. Equilibrium in the Gaseous Phase

Calculations of the equilibrium constants of reactions in gases are of considerable importance for the development of the theory of reactivity. The quantum-chemical analysis of equilibria in the gaseous phase is facilitated by two features: firstly, these processes can be sufficiently effectively studied by the methods of chemical thermodynamics, and secondly, the intermediate results of quantum-chemical calculations for many reactions can be compared with experimental data (molecular geometry, frequencies of the normal vibrations, electronic spectra, barriers to internal rotation, heats of formation, and enthalpies of reactions).

Although the basic scheme for calculating K_p in the gaseous phase is clear, its application to problems of chemical reactivity is still extremely limited. Various gaseous equilibria have been studied[72–83] on the basis of theoretical calculations of K_p with different potential functions (empirical functions, or functions found from the solution of the Schrödinger equation). Except for the case of diatomic molecules, the partition functions in the RR–HO approximation were used in all cases (see Section II.3).

In the determination of equilibrium constants by theoretical methods, the enthalpy of reaction is the most complicated characteristic to calculate. The rotational and vibrational partition functions have little influence on the accuracy of the calculation of K_p. It can be shown that an error of 3 kcal mole^{-1}, allowed in the determination of the enthalpy at low temperatures, leads to an error in the equilibrium constant which is greater by two orders of magnitude. The versions of the MO methods available at present can hardly give enthalpy values even with this clearly inadequate accuracy of ±3 kcal mole^{-1}. In 1970, the semi-empirical MINDO/2 method aroused great expectations, but it was found in the general case that this method also does not make it possible to calculate ΔH°_f with the required accuracy[84].

Nevertheless, there are a large number of reactions for which the NDO approximation can be used to carry out sufficiently accurate calculations of equilibrium constants. These calculations can be carried out directly only by the MINDO/2 method, since the CNDO/2 and INDO methods require modification[83]. (Examples can be found in papers[81,83] on the dimerisation of the radicals CH_3, NH_2, HCO, and NF_2.) In many cases the error of the determination of the enthalpy of reaction is so great that it makes it impossible to estimate equilibrium constants reliably by semi-empirical methods. At present there is no semi-empirical method which is sufficiently general and could be used to find the enthalpies of reactions with the required accuracy. The recently published MINDO/3 method[85] has not yet been thoroughly tested.

Some positive results have been obtained by semi-empirical methods. The dimerisation of NF_2 represents an equilibrium involving the isomerisation of the reagent; this feature is encountered fairly frequently, but does not usually attract attention. Tetrafluorohydrazine exists in *trans*- and *gauche*-forms

$$\begin{array}{l} 2NF_2^{\bullet} \rightleftarrows trans\text{-}N_2F_4 \qquad (10) \\ \qquad\qquad \Updownarrow \\ 2NF_2^{\bullet} \rightleftarrows gauche\text{-}N_2F_4\ . \qquad (11) \end{array}$$

The values of ΔH_0° for reactions (10) and (11) were obtained by the CNDO method[83] with modified values of the parameters; for this purpose, a number of N and F compounds having known properties were used. The optimised molecular geometries and calculated frequencies of the normal vibrations were used to calculate ΔH_T°, ΔS_T°, and the equilibrium constants of reactions (10) and (11). In the calculation of the entropy term, the existence of two optical isomers[86] of the *gauche*-form of N_2F_4 was taken into account. The values of ΔH°, ΔS°, and K_p for the equilibrium $2NF_2^{\bullet} \rightleftharpoons N_2F_4$ were calculated from Eqns. (12)–(14), in which the index "i" refers to reactions (10) and (11)[88,89]

$$K_p = \sum_{i=1}^{n} K_p^i, \qquad (12)$$

$$\Delta H^0 = \sum_{i=1}^{n} \frac{K_p^i}{K_p} \Delta H_i^0, \qquad (13)$$

$$\Delta S^0 = \sum_{i=1}^{n} \frac{K_p^i}{K_p} \left(\Delta S_i^0 + R \ln \frac{K_p}{K_p^i} \right). \qquad (14)$$

The values obtained show fairly good agreement with the experimental data.

The study of the carbon systems C_n in the vapour over graphite is of both theoretical and experimental interest. The geometry has been determined experimentally only for C_2 and C_3; for $n > 3$, a linear arrangement of the carbon atoms was first assumed[73], and for these systems the values of ΔH_0° were calculated by the simple MO method (as far as C_{17}). Later, it was established theoretically that rings are more stable than linear forms[90,91]. The study of the potential energy surfaces of several of these systems has shown, however, that the species C_n have a more complex geometric structure at the stationary points. As an illustration, Fig. 2 gives the geometry of the singlet ground state of C_4 at different stationary points of the surface. Of the seven stationary points, three are minima; the linear form corresponds to a saddle point. The thermodynamic characteristics of the reaction $4C(graphite) \rightleftharpoons C_4(gas)$ have been published[74,92].

To conclude this section, mention may be made of a systematic study[66] of the applicability of the CNDO/2, INDO, and MINDO/2 methods in the calculation of the entropy term of equilibria. It was shown that the replacement of the experimental molecular data by quantities determined by the methods of statistical thermodynamics introduces into the value of $\lg K_p$ (at temperatures below 1000 K) an error not exceeding 0.5%. This feature provides an optimistic estimate of the possibilities provided by semi-empirical methods for the calculation of K_p in the gaseous phase.

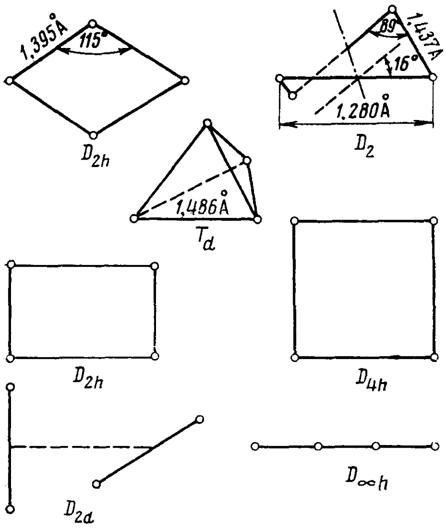


Figure 2. Configurations of the nuclei of the C_4 molecule corresponding to stationary points situated on its energy surface. For configurations in which the energy is a minimum, their symmetry groups and geometric parameters are indicated.

3. Kinetics of Reactions in the Gaseous Phase

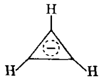
a) Static approximation

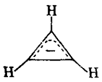
Static methods for studying chemical reactivity are based on the theory of absolute reaction rates, formulated by Eyring in the nineteen-thirties. In contrast to the case of "dynamic" methods, it is assumed that the velocity of the reacting species is so low that in the course of the reaction, energy transfer between different degrees of freedom can take place. The reaction trajectory, and hence the dependence of the geometry of the reacting species on the time measured from the start of the reaction, is replaced by the reaction coordinate, defined as the "energetically most favourable" path by which it is possible to go from the starting materials to the reaction products as a result of a continuous change in the geometry of the molecules. The change from reaction trajectory to reaction coordinate is extremely significant. The positions of the points on the reaction trajectory depend on the initial conditions—the geometries and momenta of the reacting species. Since these quantities are usually unknown (more accurately, they should be regarded as random quantities), it is necessary, in the calculation by dynamic methods, to carry out a large number of calculations for different initial conditions and to treat these results statistically. The reaction coordinate is independent of the choice of initial state of the system, and as a rule, only one reaction coordinate can be constructed for a given reaction. Thus the use of static methods leads to considerable economy in the calculations. It is necessary, however, to take account of the assumption that the reaction takes place sufficiently slowly. From this viewpoint, the extent to which the static or dynamic approximation corresponds to the conditions for the problem being studied can be estimated.

As already noted, the description of the reaction mechanism by static methods is independent of the initial conditions (the relative arrangement of the atoms and the momentum). Moreover, if various purely quantum-chemical effects, for example the tunnel effect, are neglected, it is sufficient, for the calculation of the rate constant, to know only the properties of the reacting species and the system situated on the reaction coordinate and exhibiting the highest energy. This system is called the activated complex; the difference between the energy of this complex and the energy of the original molecules is called the activation energy. If the treatment is restricted to qualitative or comparative conclusions, it is possible to estimate the reactivity of molecules by studying the properties of the starting materials. This can be done by methods using the theory of reactivity indices [7,93,94], the theory of frontier orbitals [4,96], and a whole series of methods based on perturbation theory [95,97-101]. Finally, it is possible to make qualitative estimates of the nature of a reaction without any calculations, merely on the basis of symmetry considerations, as for example in the simple version of the Woodward–Hoffman theory [9,102]. All these methods are static methods. The present review, however, will deal chiefly with methods which can be used (in principle at least) to carry out exact calculations of rate constants. These methods are based directly on the theory of absolute reaction rates.

Although accurate data on the structures of the molecules of the reacting substances are often available, there is almost no information on the structure of the activated complex. The determination of the geometry of the activated complex or of all possible activated complexes in the case where a given reaction can take place by several mechanisms is therefore a fundamental problem of the theory of absolute reaction rates. In the case of unimolecular reactions for symmetrial molecules, the study of activated complexes reduces to an analysis of the stationary points of the potential energy surfaces. This analysis can be carried out using programmes for the automatic optimisation of the geometry (see Part II).

An example is provided by the calculation of the possible structures of the excited singlet state of the cyclopropenyl anion [103]. In this case the programme for optimising the geometry gave the completely symmetrical structure (I) and also structures (II)–(VI) having a lower symmetry. System (VI) is a stable isomer; structures (III)–(V) are activated complexes. Structures (I) and (II) are neither stable isomers nor activated complexes.


(I)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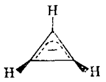
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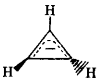
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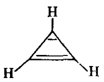
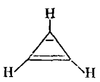

(V)


(VI)

An analogous problem was examined by Dewar and coworkers [104-106] and Komornicki and McIver [107], who did not, however, analyse the nature of the stationary points. If even qualitative information on the structure of the activated complex is available, the correct structure of the activated complex can be obtained by optimising the geometry [108].

In most cases, there is of course no reliable information on the structure of the activated complex. If however a definite structure is taken as a basis, it is always possible that there exists another activated complex, which may correspond to a lower activated energy. In the general case, it is in practice impossible to carry out a rigorous analysis of the energy as a function of all the internal coordinates of the molecule. It may be noted that for a complete description of one of the simplest reactions of the type $AB + C \rightleftharpoons A + BC$, involving only three particles, it is necessary to take account of three internal coordinates, so that in this case it is necessary to study a surface in four-dimensional space. The problem can often be simplified by assuming that only one or two internal coordinates of the molecule (bond lengths, valency angles, or twisting angles) change in the course of the reaction, while all the other coordinates remain constant. This method has been used in many cases [109-118].

This method has two important disadvantages. Firstly, it is assumed that only a small number of coordinates change in the course of the reaction. This assumption is never fully justified in practice, and it introduces an error which cannot be calculated, even approximately. Moreover, for many reactions it is impossible to describe a mechanism involving changes in only two coordinates. Secondly, when certain coordinates are distinguished, a subjective factor is introduced into the calculation; a definite reaction mechanism, not necessarily correct, is assumed a priori.

The first of these unsatisfactory features was eliminated soon after the development of methods for the automatic optimisation of the geometry. When these methods are used, allowance is made for the fact that the activated complexes correspond to points situated on the reaction coordinates; it is assumed that in the course of the reaction the system is unstable with respect to one of the internal coordinates, the so-called critical coordinate, which may be, for example, a bond length in the case of addition or dissociation, a valency angle in isomerisation, or a torsional angle in the study of barriers to rotation. A series of calculations is then carried out, in which the critical coordinate is varied in definite steps, and the other coordinates are optimised.

This technique was used by Dewar [114-116] and McIver and Komornicki [117]. The method is undoubtedly more convenient than the methods mentioned earlier, since the multi-dimensional problem is reduced to a one-dimensional problem, and involves essentially modelling of the most favourable reaction path. The coordinate of the forward reaction determined in this way usually differs from the coordinate of the back reaction, however, and neither of them passes through the point corresponding to the activated complex [117]. This "chemical hysteresis" naturally does not agree with experiment. A more significant unsatisfactory feature is the arbitrary nature of the choice of critical coordinate. In most cases this choice is based on intuition, and the chemical hysteresis may increase considerably if the choice of critical coordinate is not successful. Moreover, many reactions cannot be described satisfactorily in terms of one critical coordinate.

These unsatisfactory features were eliminated in a study [32] based on the classical idea that the reaction coordinate is described by a point which changes along a path passing through one of the troughs of the potential energy surface. The method of calculation is analogous to that in which the critical coordinate is used. The reaction coordinate is approximated successively by a series of points x_k. It is first assumed that these points are equally separated from one another. The first approximation of the $(\mu + 1)$th point $x'_{\mu+1}$ is determined from the μth point and the direction of the gradient. The position of the $(\mu + 1)$th point is then refined until the conditions formulated in the work cited[32] are fulfilled. If c_{ik} is the ith component of the kth eigenvector, E_k the kth eigenvalue of the force constant matrix, g'_j the jth component of the gradient at the μth point, and n the number of the eigenvector parallel to the gradient, the correction r_i to the ith coordinate of the point $x'_{\mu+1}$ is given by the equation:

$$r_i = -\sum_{k \neq n} E_k^{-1} c_{ik} S_k, \tag{15}$$

where $S_k = \sum_j c_{jk} g'_j$. This method makes it possible in principle to calculate all reaction coordinates and to obtain all activated complexes; the method does not exhibit chemical hysteresis.

b) Dynamic approximation

Chemical reactions represent the sum of a whole series of elementary processes taking place between atoms and molecules, as a result of which the molecules of the reagents interact with one another for a period of time, forming so-called "collision complexes", activated complexes, or transition states. If the lifetime of this system is sufficiently long ($\tau > 10^{-12}$ s), the interaction of the particles may lead to energy exchange between separate degrees of freedom. In this case the subsequent course of the elementary reactions depends chiefly on the properties of the "collision complex", and the process can be described within the framework of the theory of absolute reaction rates. In those cases where $\tau < 10^{-12}$ s, the course of the elementary process depends on the initial state of the system, and its description requires non-stationary methods. It is to be expected that "collision complexes" having a long lifetime will be more probable for systems having a large number of degrees of freedom than for systems having a small number of degrees of freedom.

The study of the dynamics of elementary chemical reactions is almost always based on the Born–Oppenheimer approximation. This problem therefore essentially breaks down into two independent problems: a) solution of the electronic Schrödinger equation and determination of the potential energy functions, which depend on the coordinates of the nuclei; and b) determination of the dynamic behaviour of the nuclei in the known potential field.

The solution of the first problem belongs to the field of quantum chemistry. The calculation of the potential energy surfaces raises a number of specific problems. The calculation must be carried out with sufficient accuracy, and the potential energy surface should provide a correct quantitative description of all possible modes of dissociation of the system, and for this it is necessary that the total energy of the system be sufficiently well determined for all internuclear distances.

At present, calculations of the ab initio type having the required accuracy can be carried out only for relatively small systems[118] (where the number of electrons does not exceed 40), and potential energy surfaces (for the ground state or the most important lower electronic excited states) have been found only for some of the simplest systems[119-127]. Considerable attention is now being paid to the problem of constructing model potentials in analytical form[128-133].

For complex systems, calculation of the potential energy surfaces is possible only by semi-empirical or empirical methods. The use of these methods is particularly attractive in those cases where it is possible to determine the potential in analytical form. The potential energy surfaces are most frequently calculated by the LEPS method (London–Eyring–Polanyi–Sato)[134-136]; the DCM method (diatomic complexes in molecules)[137,138], proposed more than ten years ago[139], has recently been used successfully.

The study of the dependence of the dynamics of a chemical reaction on the initial conditions and the form of the potential surface is a problem in the field of the quantum theory of scattering. In the stationary theory of scattering, the wavefunction $\psi(r)$ of a system of reacting particles is determined by solving the equation

$$\psi(r) = \varphi(r) - \int G(r, r') \cdot V(r') \cdot \psi(r')\, dr' \tag{16}$$

(the Lippman–Schwinger equation[140]), where $V(r')$ is the potential energy of the interaction, $\varphi(r)$ the wavefunction of the system of independent particles, and $G(r, r')$ the corresponding Green's function. For the case of elastic scattering, when the internal structure of the reacting particles remains unchanged, the Green's function can usually be found, so that the calculation of the scattering process presents no fundamental difficulty. The situation is more complicated for inelastic collisions. In this case the calculation can generally be carried out only after a number of crude approximations. The results obtained in this field have been summarised in a number of monographs[140,141] and reviews[142,143]. (The quantum theory of scattering has also been used to study various elementary chemical reactions[144-155].)

The scattering problem, even in the case of three particles, at present does not have an exact solution. One possible way of overcoming this difficulty is to replace the quantum-chemical description of the motion of the particles by the classical description. In this case, however, it must be borne in mind that certain quantum-mechanical phenomena have no analogy in classical mechanics, for example the tunnel effect or zero-point vibrational energy. From general considerations it may be concluded that the agreement between the results obtained by the two methods should improve with increase in the kinetic energy and mass of the interacting particles, and depends on the nature of the potential surface.

The classical reaction trajectories can be found by solving Hamilton's equations of motion

$$\begin{aligned} \frac{\partial H}{\partial q_i} &= -\frac{dp_i}{dt}, \\ \frac{\partial H}{\partial p_i} &= \frac{dq_i}{dt}. \end{aligned} \tag{17}$$

where q_i represents the generalised coordinates of the reacting particles, p_i the generalised momenta, and H is Hamilton's function, which in the case of purely conservative forces has the significance of the total energy of the system. These equations form a system of first order differential equations, which (for given initial conditions) can be solved by standard methods of numerical integration. The initial conditions are naturally determined by the positions of the particles and their velocities. The vibrational and rotational states of the particles are also taken into account in the initial conditions. The values of the coordinates and momenta obtained from the solution of the system of equations (17) can be used to determine firstly the nature of the reaction and secondly the state of the reaction products. In order to use these calculations to interpret experimental data, it is necessary to find a sufficiently large number of trajectories, corresponding to different initial conditions and modelling the real conditions statistically. A detailed analysis of the problem of the collision of three particles was carried out by Karplus and coworkers[156].

The application of the method of classical trajectories to systems having a large number of particles presents no fundamental difficulties[157] if the reaction takes place under adiabatic conditions. A number of processes take place under non-adiabatic conditions, however. Typical reactions of this kind are, for example, reactions involving the transfer of charge or of electronic energy, or spin-forbidden reactions. In the case of non-adiabatic reactions, the important regions are those in which several potential surfaces are situated fairly close to one another; this leads to considerable interaction between different states. Examples of this type of interaction are non-adiabatic electron–nuclear interactions or spin–orbital coupling. Considerable attention has been and is being paid to the calculation of these effects and the probabilities of transitions between different surfaces[158–160]; from these studies it is possible to modify the method of classical trajectories in such a way that it can be used to carry out calculations for non-adiabatic reactions[161].

The method of classical trajectories is used to solve the following problems:

a) for the theoretical estimation of various experimentally observable quantities[162–164]: the total reaction cross-section (or reaction rate constant), angular distributions and energy distributions of the products, etc.;

b) to study the influence of the nature of the potential surface and the states of the reagents on the reaction cross-section[165–169];

c) for comparison with the results of calculations by other methods[170–177] (in quantum mechanics, theory of absolute reaction rates).

Finally, the method of classical trajectories has been successfully used to study a number of reactions[162–164, 178–203].

4. Equilibrium in Solution; Solvation Energy

The properties of molecules in the gaseous phase often differ from the properties in the liquid phase. This difference is due to the interaction between the molecules of the solute and solvent. Depending on the nature of the medium, it is convenient to distinguish two types of interaction—specific and non-specific[204]. In non-specific solvation, no allowance is made for the specific characteristic features of the molecules of the solvent, which is regarded as a uniform and isotropic medium, characterised by various macroscopic constants, such as the dielectric constant or refractive index. Within the framework of this model, the energy of solvation is defined by the following equation, derived by Born[205]:

$$\Delta G = -\frac{q^2}{2r_0}\left(\frac{1}{\varepsilon} - 1\right), \qquad (18)$$

where ϵ is the dielectric constant of the solvent, q the charge of the ion, and r_0 the radius of the ion. The theory of the continuous model of a solvent was developed in more detail by Onsager[206] and Kirkwood[207]. These methods, however, make it possible to estimate only the magnitude of the solvation energy. Recently, several methods have been proposed[208–212], based on specific allowance for solvent effects directly in the Hamiltonian. These methods make it possible to take account of the influence of the solvent on those properties of the molecule which can be studied by quantum-mechanical methods. The disadvantages of the continuous model of a liquid have been discussed in detail[204].

In specific solvation, allowance is made for the specific characteristic features of the molecules of the solute and solvent. Interactions of this type are studied using models consisting of the molecules of the solute and an ordered set of solvent molecules. These systems are regarded as supermolecules, and studied by the methods of quantum chemistry. In practice, this procedure involves a number of difficulties: 1) the arrangement of the solvent molecules relative to the solute molecule is not known; 2) an appropriate potential has to be chosen for calculating the energy of interaction; and 3) usually, only the primary§ solvation shell is taken into account. These difficulties can be considered in more detail.

1. The determination of the structure of the primary or secondary solvation shells is very difficult. The experimental data can be used to estimate in a number of cases[213] only the number of solvent molecules in the primary solvation shell. This problem is unlikely to be solved for polyatomic molecules in the near future. The only possibility remaining is to model the solvation shell theoretically. In principle, this can be done by three methods: a) by using the Monte Carlo method to determine the most stable structures consisting of a given number of solvent molecules; b) to optimise, by a standard method, the structure of the entire solvation shell consisting of a given number of solvent molecules; and c) to study not the entire solvation shell, but only the part interacting most strongly with the solute molecule. All three methods have advantages and disadvantages. The Monte Carlo method is most appropriate, but even for small solute molecules the use of this method involves a considerable expenditure of machine time, even on modern fast computers. The second method can give valuable information on solvation for the expenditure of much less machine time. The third method can also be used for large molecules, but it must be borne in mind that this method can be used only to study some properties of the solvated molecule, for example the spectra or the conformation.

2. In the selection of the interaction potential, the entire structure of the molecules of the solute and solvent must first be taken into account. For the calculation of the energy of interaction it is possible to use all available methods—empirical, semi-empirical, and non-empirical. Brief mention may be made of some of the most promising methods.

Ab initio methods have been used to study the structures of various models of solvation layers. Mention may be made first of all of the work of Clementi and coworkers[214], who studied the hydration of various ions (Li^+, Na^+, K^+, F^-, and Cl^-). Here, the potential was determined by calculations of the Hartree–Fock type, after which the Monte Carlo method was used. It is very difficult to compare theoretical calculations of solvation energies with

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§The primary solvation shell consists of those solvent molecules which interact directly with the solute molecule.

experimental data. The calculated enthalpies of the complexes of the ions with 1, 2, 3, etc. water molecules show fairly good agreement, however, with mass-spectrometric data [215,216]. One method for the direct confirmation of calculations of solvation energies is by comparing the theoretical and experimental radial distribution functions. Best agreement in the case of water was obtained in a study [217] using a two-particle potential, defined in the Hartree–Fock approximation with allowance for correlation energy. For ion–H_2O complexes, unfortunately, there are no published experimental estimates of the corresponding partition functions.

The method of Clementi and coworkers [214] is fairly well founded from the physical viewpoint, but as a consequence it is used at present only for the study of the hydration of ions and small molecules. In the case of polyatomic systems, it is practically impossible to study the supermolecule either in the Hartree–Fock approximation or by the Monte Carlo method.

In a study of the hydration of the Li^+ ion, Kollman and Kuntz [218] estimated the total energy of the complexes $Li^+ + nH_2O$ ($n = 2, 4, 6$) from the $Li^+...OH_2$, $Li^+...(OH_2)...(OH_2)$, and $OH_2...OH_2$ potentials. In this way, the authors cited were able to avoid the need to examine the complex as a whole. The electrostatic model (see below) was used to take account of the H_2O molecules in the secondary and tertiary hydration shells. It was shown that the central ion influences the arrangement of the molecules in the tertiary hydration shell. The use of two-particle and three-particle potentials for a definite geometry of the solvation shell is at present the only available method for calculating the solvation energy of polyatomic systems. Complete allowance for the entire solvation shell and solvate molecule is extremely complicated, and the calculations have been carried out only for small systems.

Pullman and coworkers [219] developed a method in which only part of the solvation shell is studied. This method is based on the determination of the most stable complexes containing a small number of solvent molecules. Various properties of the solvated molecules, such as the conformation or the spectra, can be interpreted using a complex of this type. An example is provided by the results of studies of the conformations of the histamine mono- and dications by the PCILO method (see below) [220]. The isolated molecule exists in only one conformation—*gauche* in the case of the monocation and *trans* in the case of the dication. From ab initio calculations it was found that in aqueous solution the monocation can exist in both the *gauche* and *trans* forms; in the case of the dication, the *gauche*-isomer may accompany the *trans*-isomer. These results agree with experiment.

Semi-empirical methods have been used to calculate the solvation energies of ions and simple systems. In most cases the solvation layer and the central ion were regarded as a supermolecule. Good results were obtained for the hydration of ions (ion–polar molecule interaction [221-224]). The study of solvation in non-polar systems at a semi-empirical level is unlikely to succeed. It has recently been shown that the results obtained in the study of the conformation of molecules and the interactions between molecules using the semi-empirical PCILO method show good agreement with the results of calculations by ab initio methods [225]. The PCILO method is apparently the most promising method for the study of the influence of the solvent on the properties of solvated molecules.

In conclusion, brief mention may be made of a simple method for estimating the energy of interaction for polar or charged systems, based on the electrostatic approximation [226]. From the wavefunctions of two systems it is possible to estimate the energy of their electrostatic interaction and to determine their relative arrangement, corresponding to the potential energy minimum. The positions in a molecule most favourable for electrophilic attack by a point particle carrying a positive charge are often of interest. From the wavefunction (non-empirical or semi-empirical) of the corresponding molecule, the electrostatic potential at the point r_i can readily be determined from the equation:

$$V(r_i) = -\sum_{q,s} P_{qs} \cdot \int \frac{\chi_q(1)\,\chi_s(1)}{r_{i1}}\, d\tau_1 + \sum_{\alpha} \frac{Z_\alpha}{r_{\alpha i}}, \qquad (19)$$

where $\chi_q(1)$ and $\chi_s(1)$ are the AO; P_{rs} is the element of the density matrix corresponding to these AO; Z_α the charge of the nucleus of the atom α; and $r_{\alpha i}$ and r_{i1} represent respectively the distances from the point r_i to the nucleus α and to the electron. By connecting points at which the values of the potential are equal, it is possible to obtain isopotential surfaces, which give a clear description of the possible directions of electrophilic attack.

3. Kollman and Kuntz [218] used the SCF method (ab initio) to study the hydration of the Li^+ ion. It was shown that the tetrahedral structure of the primary hydration shell is energetically most favourable, and that the hydration energy is 107 kcal $mole^{-1}$. The energy of the interaction of the Li^+ ion with the water molecules of the secondary and even the tertiary hydration shells is fairly high: in the first case it is equal to 80 kcal $mole^{-1}$, and in the second case it amounts to almost 20% of the total hydration energy (the experimental value is 228 kcal $mole^{-1}$). Here it must be borne in mind that the energy of the interaction of the Li^+ ion with water is unusually high. In the case of the hydration (or solvation) of neutral molecules, it is to be expected that allowance for only the primary or secondary hydration (solvation) shells will not introduce a large error into the calculation of the energy of hydration (or solvation).

5. Kinetics of Reactions in Solution

The calculation of the rate constants of reactions in solution is an extremely complex problem [227-230]. The development of the theory of chemical reactions in the gaseous phase [231] will obviously facilitate the successful solution of this complex problem. In general, however, the methods of studying reactions in the gaseous phase can hardly be applied directly to the study of reactions in solution. It is only in the case of relatively weak interactions between the molecules of the reactants and the activated complex on the one hand and the solvent on the other hand that these methods can lead to correct semi-quantitative results.

6. Catalytic Reactions

The methods of quantum chemistry used in catalysis can be divided into two groups [232]. The first group consists of the methods of solid state physics [233-244]. For catalysis, information on the states of the electrons on the catalyst surface (surface states) are most important, since their symmetry and energy can give information on the course of the adsorption. The bulk and surface states can be studied without particular difficulty in the case of the ideal lattice of a semi-infinite crystal. Unfortunately, deviations from the ideal lattice (for example in the surface layer) and the presence of defects and chemisorbed molecules introduce considerable difficulties.

The second group consists of various methods in the quantum chemistry of molecules. The most promising methods for the solution of problems in catalysis are those which take account of all the valency electrons (semi-empirical methods of the CNDO and EHM type). The methods of this group can be used to study small systems comparatively easily, so that the catalyst is usually modelled by a system consisting of several atoms. The quality of the theoretical study of a catalytic process depends on the reliability of the quantum-chemical approximation and on the model of the catalytic reaction used.

Chemical reactions in the presence of a catalyst usually take place in several stages, the first of which is the interaction of the molecules of the original reagents with the catalyst (the formation of an adsorbate–catalyst complex, A–C). This first stage has been studied by many workers in different systems. Mention may be made of several studies[245-258] of the adsorption chiefly of diatomic molecules on the surfaces of transition metals and oxides. The authors cited obtained a model of the solid state by considering a part of a crystal consisting of several tens of atoms (three-dimensional model) or a part of the surface of the crystal (two-dimensional model), or considered only one metal atom (or one molecule of the oxide). Most calculations have been carried out by the simplest version of the EHM.

Several procedures can be used in the study of a catalytic reaction by the methods of quantum chemistry. The most fully developed of these involves the calculation of the potential energy surface for the system consisting of the atoms of the adsorbate and catalyst. Because of the complexity of the calculations, however, this approach can be used only for the simplest reactions[258-260]. For the study of systems of chemical interest, it is possible to use a simpler method involving the calculation of the electronic structure, geometry, total energy, and various other physical characteristics of A–C systems for assumed intermediate products and possible activated complexes[261,262]. The reliability of the information on the catalytic process obtained in this way depends to a considerable extent on the choice of the model for the reaction, that is on the assumptions regarding the intermediate products or activated complexes. The third and most economic method is based on the calculation of the electronic structure of the complex A–C. The reactivity of this complex is estimated using quantum-chemical indices of reactivity[263] or orbital symmetry conservation rules[264-267].

From the foregoing it follows that in the study of a catalytic reaction by the methods of quantum chemistry, the description of the catalyst presents the greatest difficulty. A model of the catalyst, taking account of its surface or bulk properties, should consist of a large number of atoms, and this complicates the calculation considerably. Moreover, in these models, allowance is made for crystal lattice defects. Another no less important problem concerns the quality of the quantum-chemical approximation. Non-empirical methods are in practice inapplicable to the solution of problems of catalysis, because of the complexity of the systems. Even without considering the problem of the parametrisation of semi-empirical methods for transition metals, the use of these methods to study the reactivity of systems containing a model of the catalyst with a large number of atoms still lies beyond the computing facilities of most laboratories. Thus at present the reactivity of a complex A–C can in most cases be studied only by means of the EHM, which suffers from a fairly large number of disadvantages. Even this method, however, can be used to study the potential energy surface or any cross-section of this surface only for the simplest catalytic reactions.

Thus the problems associated with taking explicit account of the catalyst are related to the specific features of the methods of quantum chemistry and difficulties of computation. In this connection, in the study of a catalytic reaction, the catalyst is taken into account implicitly as a perturbation of the adsorbate. The reactivity of this adsorbate can be studied by standard methods of quantum chemistry.

The results of the theoretical analysis and the experimental data, discussed in more detail elsewhere[232,268], indicate that the interaction of an adsorbate with a catalyst is accompanied by the transfer of electron density from a bonding MO of the adsorbate to a vacant MO of the catalyst, and also from a filled MO of the catalyst to an antibonding MO of the adsorbate. The degree of electron density transfer is determined by the electronic structure of the adsorbate and catalyst. When the transfer of charge is approximately the same in both directions, the state of the adsorbate is analogous to the excited state of the isolated molecule, or the superposition of several excited states. In charge transfer, the frontier orbitals of the interacting systems usually play the most important roles, so that it may be assumed that the state of the adsorbate corresponds to the first excited state. An example is provided by the interaction of a two-electron adsorbate (for example H_2) and a two-electron catalyst (this model can be used to study the interaction of the frontier orbitals of a many-electron adsorbate and a many-electron catalyst) (Fig. 3*a*). If φ^A represents a filled MO and φ^B a vacant MO of the adsorbate, and ψ^B and ψ^A represent filled and vacant MO of the catalyst respectively (the superscripts A and B characterise the symmetry of the MO), the MO of the complex A–C has the form:

$$\begin{aligned}\Phi_1^A &= c_1^A\varphi^A + c_2^A\psi^A,\\ \Phi_2^B &= c_1^B\psi^B + c_2^B\varphi^B,\\ \Phi_3^A &= c_1^A\psi^A - c_2^A\varphi^A,\\ \Phi_4^B &= c_1^B\varphi^B - c_2^B\psi^B.\end{aligned} \qquad (20)$$

$(c_2^A)^2$ then provides a measure of the transfer of electron density from the adsorbate to the catalyst (from the MO φ^A to the MO ψ^A), and $(c_2^B)^2$ the transfer of electron density from the catalyst to the adsorbate (from the MO ψ^B to the MO φ^B). The difference $(c_2^A)^2 - (c_2^B)^2$ characterises the charge on the adsorbate, and the smaller of the squares of these coefficients gives the degree of excitation of the adsorbate. If one of the coefficients is much greater than the other (see Figs. 3*b* and 3*c*), charge transfer takes place in only one direction. In extreme cases, when $c_1^A \simeq 1/\sqrt{2}$, $c_2^A \simeq 1/\sqrt{2}$ and $c_1^B \simeq 1$, $c_2^B = 0$, a radical-cation is formed, and when $c_1^B \simeq c_2^B \simeq 1/\sqrt{2}$ and $c_1^A \simeq 1$, $c_2^A \simeq 0$, a radical-anion is formed.

It may thus be expected that the reactivity and various other physical properties of the adsorbate in the complex A–C corresponds qualitatively to the properties of radical-ions or an excited state of the adsorbate. Here, the following points should be borne in mind:

a) only "part" of the electron density is transferred from the metal atom to the ligand;

b) the donor and acceptor powers of the adsorbate with respect to the metal atom are usually different, so that quantitatively, the decrease in the population of the bonding MO is different from the increase in the population of the antibonding MO;

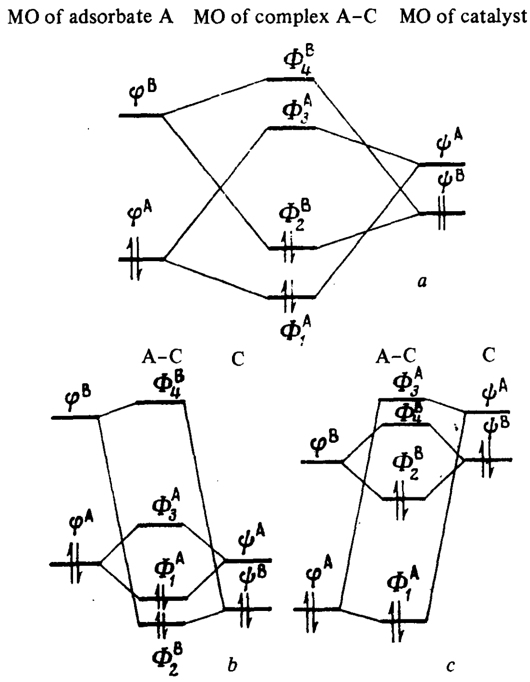


Figure 3. Interaction of the molecular orbitals of the adsorbate (A) and catalyst (C): *a*) for the formation of a partly excited state of the adsorbate ($c_2^A \simeq c_2^B$); *b*) for localisation of the positive charge on the adsorbate ($c_2^A \gg c_2^B$); *c*) for localisation of the negative charge on the adsorbate ($c_2^B \gg c_2^A$).

c) charge transfer takes place not only from the highest filled MO, but also from other orbitals, Moreover, there may be changes in the population of other vacant MO (although the frontier orbitals probably play the chief role in this process);

d) in this model, no allowance is made for the specific characteristic features of the catalyst surface.

The potential at the catalyst surface, which may lead to appreciable changes in the electronic structure of the adsorbate, is of considerable importance in heterogeneous catalytic processes. A strong electrostatic field may lead to appreciable decrease in the strength of the bonds of the adsorbate[269,270]. Moreover, allowance must be made for the fact that the magnetic moments of the atoms of the catalyst also influence the course of the reaction.

Comparison of catalytic and non-catalytic reactions.

Catalytic reactions	Non-catalytic reactions
Reactions catalysed by electron-acceptor systems (for example metal oxides)	Reactions of radical-cations and reactions taking place in the source of a mass spectrometer (cationic mass spectrometry)
Reactions catalysed by electron-donor systems (for example alkali metals)	Reactions of radical-anions and reactions taking place in the source of a mass spectrometer (anionic mass spectrometry) (Ref.271)
Reactions catalysed by systems in which the back-donation mechanism occurs (transition metal atoms and ions)	Reactions of electronically excited particles (photochemistry)
Reactions influencing the catalyst surface; the action of its force field	Reactions in an external electric or magnetic field

The mechanism of the effect of the catalyst on the adsorbate described above have analogies in other fields of chemistry (see Table). The analysis of catalytic reactions can therefore be facilitated by studying these processes, involving radical-ions (radical reactions,

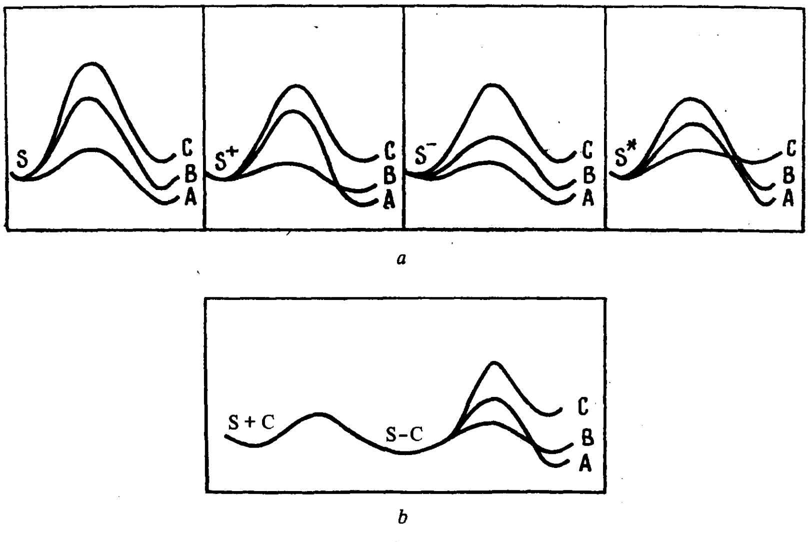
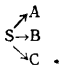


Figure 4. Section of the energy surface: *a*) for the molecule of a hypothetical substance S, for the radical-cation S^+, for the radical-anion S^-, and for the excited state S^*; *b*) for the catalytic reaction.

cation and anion mass spectrometry) and molecules in excited electronic states. In the theoretical study of catalytic processes, the state of the adsorbate in the A–C complex can be modelled either by an appropriate radical-ion or by an excited electronic state[232], depending on the nature of the catalyst. This procedure makes it possible to use more fully developed quantum-chemical methods than in the case where explicit account is taken of the catalyst. The quality of the results naturally depends on the extent to which the model corresponds to the actual state of the adsorbate interacting with the catalyst.

The similarity between catalytic processes on the one hand and radical or photochemical reactions on the other makes it possible to determine beforehand the appropriate type of catalyst for carrying out the reaction. Fig. 4*a* gives the cross-sections of the potential energy surface of a molecule of a hypothetical substance S, its ions S^+ and S^-, and its excited state S^*. It is assumed that the transformation of the substance S can take place according to the following scheme:



It is assumed that analogous processes are possible for other forms of the adsorbate. Comparison of the activation energies (see Fig. 4) shows that the decomposition of the substance S (S^+, S^-, or S^*) gives the products A for S and S^-, B for S^+, and C for S^*. If it is desired to use a catalyst to obtain, for example, product B, it is necessary to use a catalyst with strong electron-acceptor properties. The cross-sections of the corresponding surface for the S–C complex for a catalyst of this type are shown in Fig. 4*b*. If on the other hand the products of the catalytic transformation of the substance S are known, it is possible to determine, from the known reactivity of the radical-ions and excited states of the adsorbate, how the catalyst influences the adsorbate.

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Advances in the Study of the Chichibabin Reaction

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The state of research into one of the most important reactions of heterocyclic compounds—their amination by sodium amide (the Chichibabin reaction)—is described. The mechanism of the reaction, its application to specific classes of nitrogen-containing heterocycles, and certain reactions related to the Chichibabin reaction, namely amination of heterocycles by organic derivatives of metal amides, substitutional amination with elimination of hydrocarbon groups, amination of *N*-heteroaromatic cations, and hydrazination and hydroxylation, are discussed.
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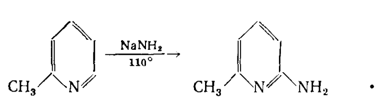
I. INTRODUCTION

In 1914 Chichibabin and Zaide reported that, when they attempted to metallate the CH_3 group of α-picoline by sodium amide in toluene, they unexpectedly observed the amination of the pyridine ring in the free α-position[1]:



Later Chichibabin and his students extended this amination method to many pyridine, quinoline, and isoquinoline derivatives. The Chichibabin reaction has had an enormous influence on the development of the entire chemistry of pyridine and has acquired great practical importance. Its application to condensed imidazole systems, achieved for the first time by Simonov and coworkers[2], proved to be particularly fruitful. A view widely expressed in textbooks and reference literature (see, for example, Surrey[9]) is that the Chichibabin reaction is most typical for pyridine and its benzologues. Nevertheless, we shall show that this is not altogether the case.

There exist two fundamental reviews on the Chichibabin reaction[3,4]. The first, published more than 30 years ago, is naturally obsolete. The second has unfortunately remained little known and since its publication many fundamental new data concerning this reaction have accumulated in the literature. In a number of other reviews the discussion is restricted to reactions of pyridine[5-7] or imidazole[8] derivatives.

The aim of the present review is to give an account of the present state of research into the Chichibabin reaction and certain related reactions, primarily processes such as hydroxylation of heterocycles by alkalies and their hydrazination by metal hydrazides. The review reflects as far as possible the entire literature on the given problem published up to 1st June, 1976.

II. REACTION MECHANISM

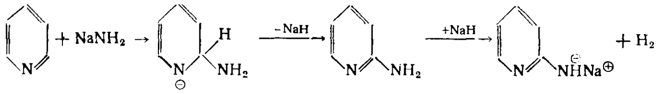
Owing to the high basicity of the amide ion, the Chichibabin reaction is usually carried out in aprotic solvents inert with respect to $NaNH_2$. Aromatic hydrocarbons, dimethylaniline, and liquid paraffin are most commonly used. Sodium amide is almost insoluble in these solvents, so that the reaction takes place under heterogeneous conditions. The only solven in which $NaNH_2$ (and to a greater extent KNH_2) is soluble proved to be liquid ammonia[10]. The Chichibabin reaction in liquid ammonia, achieved for the first time by Bergstrom[11-15], requires specific conditions: the use of sealed tubes and a long process time (up to several days); at the same time it is difficult to follow the course of the reaction. Furthermore, many heterocycles (pyridine, condensed imidazoles, etc.) are not aminated in liquid ammonia. The Chichibabin reaction can be carried out also without a solvent, in the melt, but this usually leads to less satisfactory results. In most instances the reaction begins at a comparatively high temperature (100–130°C), which is regulated in such a way that the evolution of hydrogen (a characteristic feature of amination) is uniform.

The mechanism of the Chichibabin reaction has been studied much less than those of other nucleophilic substitution reactions and is still not entirely clear. This is to a large extent due to the difficulty of studying the reaction kinetics (specificity of the conditions and occasional formation of side products). However, studies have been published recently on the reaction kinetics, based on the measurement of the rate of evolution of hydrogen[16-18].

In broad outline, the reaction involves the substitution of a hydride ion in the α- or γ-position in azaheterocycles by an amino-group. Two different mechanisms of the Chichibabin reaction have been discussed in the literature; —"addition-elimination" and "elimination-addition" (the heterocyclic aryne mechanism).

1. THE "ADDITION-ELIMINATION" MECHANISM

In 1930 Ziegler and Zeiser[19] proposed a two-stage reaction mechanism, the first stage involving the formation of an addition product I and the second its aromatisation to the 2-amino-derivative (II) as a result of the elimination of sodium hydride. It was suggested that NaH immediately reacts with the amino-group, which leads to the formation of the sodium salt of the amine (II) and the evolution of hydrogen:



(I) (II) (III) (1)

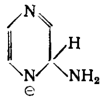
Although the main idea of this mechanism has been generally accepted[5,20,21], it has not been specified in detail and does not explain many experimental facts. Thus, as regards the addition stage, the mechanism does not provide an answer to the following questions: (1) whether sodium amide adds to the C= N bond synchronously or in stages; (2) if the addition takes place in stages, does the coordination of the $Na^{\oplus}$ ion to the pyridine nitrogen atom or the addition of $NH_2^{\ominus}$ to the carbon atom in the 2-position take place first; (3) do other intermediates, for example, radical-anions, etc., participate in the addition stage. There is similar uncertainty as regards the aromatisation stage (see below). It is not surprising that the Ziegler mechanism has no predictive power and cannot explain why some heterocycles are aminated while others, with a similar structure, are not.

Experimental facts which throw light on the mechanism of each reaction stage separately are discussed below.

(a) The Additional Stage

The formation of the σ-complex. For a long time the formation of anionic σ-complexes (I) was accepted without proof, although analogous adducts with sodium hydrazide[22], lithium tetrahydroaluminate[23], and phenyl-lithium[24] have been described.

Deeply coloured adducts of certain azines and diazines with sodium and potassium amides [compounds (IV)–(VII)] were detected recently in liquid ammonia by ^1H NMR:[25,26]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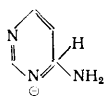
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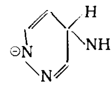
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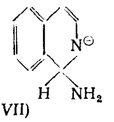
(VII)

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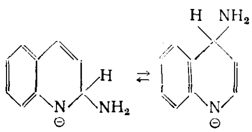
The σ-complexes (IV)–(VII) are formed almost instantaneously. Judging from their dissociation constants ($K \leq 10^{-5}$), the addition under these conditions is almost irreversible. It was not possible to isolate the complexes in a crystalline state[11–15,25,26]. Two σ-complexes, formed under kinetically [compound (VIII)] and thermodynamically [compound (IX)] controlled conditions, were discovered for quinoline


(VIII) (IX)

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There is no doubt that σ-complexes are also formed on amination under heterogeneous conditions. Thus in the reaction involving isoquinoline the red colour characteristic of the σ-complex (VII) in liquid ammonia appears on amination in xylene and dimethylaniline. In general the appearance of a deep, frequently red, colour is a characteristic feature of the Chichibabin reaction.

Quantum-mechanical reactivity indices. Bearing in mind the nature of the Chichibabin reaction, it is logical to suppose that the carbon atom with the lowest positive charge q^+ is attacked first by the amide ion. Tables 1 and 2 present the values of q^+ for certain azines and azoles.

Quantum-mechanical calculations on the Chichibabin reaction are of dual importance. On the one hand, one can compare with their aid the reactivities of various positions within the same molecule (for example the α- and γ-positions in the pyridine and quinoline molecules) and, on the other hand, the electrophilic properties of a specific centre can be compared in different heterocycles.

Table 1. The positive charges on the carbon atoms, the basicities, and the reactivities of azines.

Compound	Position	π-Electronic charge (Ref.27) (Hückel MO method)	σ + π charge (Refs.28,29) (CNDO/2 method)	pK_a^{30}	Behaviour w.r.t. $NaNH_2$
Pyridine	2	0.077	0.102	5.23	+
	4	0.050	0.041		+–
Quinoline	2	0.104	0.090	4.94	+
	4	0.068	0.035		+–
Isoquinoline	1	0.105	0.066	5.40	+
	3	0.053	0.077		–
Benzo[*f*]quinoline	2	0.095	—	5.15	+
	4	0.059	—		–
Acridine	9	0.105	0.011	5.61	+–
Phenanthridine	6	0.133	—	4.52	+
Pyridazine	3 (6)	0.077	0.061	2.33	–
	4 (5)	0.047	0.017		–
Pyrimidine	2	0.155	0.156	1.30	+–
	4	0.126	0.115		–
Pyrazine	2,3,5,6	0.074	0.058	0.065	+–
1,3,5-Triazine	2,4,6	0.203	0.183	1.0	–
Quinazoline	2	0.073[31]	0.156	3.51	–
	4	0.064[31]	0.116		+
Quinoxaline	2	0.097	0.060	0.56	–

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*The + sign means readily aminated, the +– sign means aminated with complications, and the – sign means not aminated.

Table 2. The positive charges on the α-carbon atom, the basicities, and the reactivities of azoles.

Compound	π-Electronic charge (Ref.27) (Hückel MO method)	σ + π charge (Ref.28) (CNDO/2 method)	pK_a^{30}	Behaviour w.r.t $NaNH_2$*
Imidazole	0,094	0.110	7.33	–
4,5-Diphenylimidazole	0.107	—	5.90	–
Phenanthroimidazole	0.137	—	—	–
Benzimidazole	0.170	0.158	5.52	+
Imidazoä4,5-*b*]pyridine	0.170	—	3.95	–
Purine	0.172	0.179	2.39	–**
Naphtho[1,2,-*d*]imidazole	0.152	—	5.28	+
Naphtho[2,3-*d*]imidazole	0.186	—	5.24	+
Imidazo[4,5-*b*]phenazine	0.202	—	3.62	–
Perimidine	0.256	0.198[32]	5.90	+
Indazole	0.063	—	1.27	–

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*For the significance of the notation, see the footnote to Table 1.

**An attempt was made to aminate 9-ethyl-6-dimethylaminopurine (pK_a = 3.90)[27].

The results sometimes depend significantly on the chosen method and parameters. For example, in the calculation by the Hückel molecular orbital method the highest positive charge in the isoquinoline molecule is found in the 1-position, while calculation by the CNDO/2 method shows that it occurs in the 3-position (Table 1). Comparison of experimental data and the results of the calculations leads to the following conclusions.

1. For the successful amination of the heterocyclic compound, it is necessary that the α-carbon atom in its molecule should carry a fairly large positive charge. Thus indazole, imidazole, 4,5-diphenylimidazole, and phenanthreno[9,10-*d*] imidazole†, which do not possess a sufficiently high charge, are not aminated.

2. A high positive charge by itself does not guarantee successful amination. For example, purine, imidazo-[4,5-*b*]pyridine, and imidazo[4,5-*b*]phenazine, which are not aminated, carry a positive charge which is comparable to that in the readily aminated benzo- and naphtho-imidazoles.

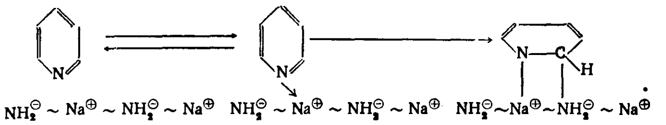
3. The site of attack by the amide ion does not always coincide with the location of the highest positive charge. For example, quinazoline is aminated in the 4-position and not the 2-position [33].

4. The employment of the energies of anionic localisation as reactivity indices is also unsatisfactory. Thus the values of L_2 and L_4 for pyridine (2.35 β and 2.37 β) and quinoline (2.24 β and 2.13 β) are non-informative and agree poorly with experiment [27,34].

The role of the basicity of the heterocycle. In principle, the Chichibabin reaction may be regarded as the interaction between the nitrogen-containing heterocycle and the amide ion, disregarding the influence of the counterion [35]. In amination in liquid ammonia, which ionises the M$-$NH$_2$ bond [10], such simplification is permissible‡, which is demonstrated, particularly, by the absence of a relation between the basicity of the heterocycle and its ability to be aminated in liquid ammonia.

On the other hand, in amination under heterogeneous conditions there is a distinct relation between the basicity of the compound and its ability to be aminated by metal amides [4,36]. Compounds whose basicity is in the range $pK_a = 5-6$ are most readily aminated; they include benzo- and naphtho-imidazoles, pyridine, isoquinoline, benzo[*f*]quinoline, and many others. Weakly basic diazines, triazines, quinoxaline, and certain imidazole systems are poorly aminated or do not react with NaNH$_2$ at all (Tables 1 and 2). The Chichibabin reaction is most sensitive to variations in basicity in the series of azoles [36-40]. Inspection of extensive experimental data shows that the lower limit of the basicity of benzimidazole derivatives which can be aminated lies in the range $pK_a = 4.2$ to 4.3. [27,36]

In order to account for the influence of basicity, it has been suggested that the pyridine nitrogen atom undergoes preliminary coordination to the sodium cation [4,36]. Such coordination not only orients the heterocycle at the NaNH$_2$ surface but also greatly increases the positive charge on the α-carbon atom, facilitating thereby the addition of the amide ion to the latter:



(X) (XI) (XII)

It has been shown by infrared spectroscopy that the sorption and coordination processes are reversible and precede the formation of the σ-complex [4,27].

If the $\gtrdot N \rightarrow NaNH_2$ coordination is regarded as the first stage of the Chichibabin reaction, then presumably more basic heterocycles should be aminated more readily. However, this happens only up to a certain limit. The point is that, with increase of basicity, the position charge on the α-carbon atom decreases synchronously. For successful amination, the optimum combination of pK_a and q_{α}^{+} is evidently necessary [4,36]. Heterocycles with $pK_a = 5-6$ evidently meet this requirement. Incidentally, there are also other exceptions, which will be discussed later. More basic heterocycles ($pK_a > 6-7$) do not enter into the Chichibabin reaction or are aminated with much difficulty. These include, in particular, imidazole [4] and 4- and 5-azaindoles [41]. The most basic of all the compounds which are successfully aminated is 4-dimethylaminopyridine ($pK_a = 9.37$), which reacts with NaNH$_2$ under extremely severe conditions and the yield of the 2-amino-derivative is low [41].

The hypothesis of the coordination of the pyridine nitrogen atom to the Na$^+$ ion helps to explain, apart from the influence of basicity, a number of other interesting features of the Chichibabin reaction, primarily the difficulty of γ-amination under heterogeneous conditions and the so-called *ortho*-dimethoxy-effect.

Characteristics of γ-amination. The possibility of γ-amination is determined mainly by two factors: the relative activities of the α- and γ-positions and the reaction conditions (homogeneous and heterogeneous). It must be emphasised that, when both positions are free, the reaction is predominantly directed to the α-atom. If the α-positions are occupied, the reaction is directed to the γ-position (the 4-position). For example, on amination in liquid ammonia, quinoline forms a mixture of 2- and 4-aminoquinolines in proportions of 6 : 1, [13] while 2-phenylquinoline [15] and quinoline-2-carboxylic acid [42] are aminated under the same conditions in the 4-position with an almost quantitative yield. Successful γ-amination under homogeneous conditions is, incidentally, not surprising, since metal amides are highly dissociated in liquid ammonia [10] and the ratio of the isomers is determined mainly by the relative reactivities of the α- and γ-carbon atoms.

On the other hand, under heterogeneous conditions, after the $\gtrdot N \rightarrow NaNH_2$ coordination, the γ-position becomes relatively inaccessible to the amide ion for geometrical reasons and the yield of the isomer is greatly reduced. Indeed, γ-amination of quinoline under heterogeneous conditions has not been observed. 2,6-Dimethylpyridine is converted into 4-amino-2,6-dimethylpyridine with a yield of only 6%. [43]

Acridine in a very convenient compounds for the study of γ-amination. In liquid ammonia 9-aminoacridine was obtained in a high yield [42], but in dimethylaniline the yield

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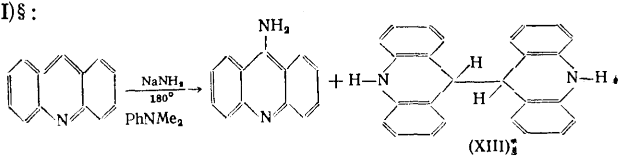
† Here, and henceforth in the discussion of the ability of azoles to be aminated we have in mind the behaviour of their *N*-substituted derivatives in relation to sodium amide.

‡ However, Bergstrom showed that, even under these conditions, the nature of the cation influences the reaction. Thus quinoline is more effectively aminated in liquid ammonia with the aid of Ba(NH$_2$)$_2$ than KNH$_2$. [12-15]

fell to 31%[44] and the main product became 9,9′-biacridanyl (XIII)§:

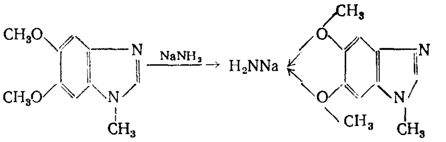


(XIII)§

Since the pK_a and q_γ^+ values for acridine favour the Chichibabin reaction (Table 1), the low yield of the amine can be accounted for only by the separation of the amide ion and the γ-position in the adsorption complex.

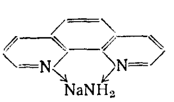
The *ortho*-dimethoxy-effect (ODE). In the study of the Chichibabin reaction involving the benzimidazole series it was observed that compounds containing methylenedioxy- or *ortho*-dimethoxy-groups cannot be aminated under a wide variety of conditions regardless of the site in the molecule containing the *ortho*-dimethoxy-group[39,46]. On the other hand, compounds with separated methoxy-groups are aminated to a satisfactory yield.

In order to account for the ODE, it has been suggested that *ortho*-dimethoxy-derivatives are sorbed on the NaNH$_2$ surface with formation of complexes of type (XIV),[39,46] which cannot be aminated further owing to their unfavourable orientation in relation to the C=N bond (ultimately one of the methoxy-groups is demethylated with formation of the corresponding phenoxide ion, which is inert with respect to NaNH$_2$ [46,47]). This explanation of the ODE has been confirmed by data for azacrown-ethers, which give rise to complexes with alkali metal ions via oxygen and not nitrogen atoms (in consequence of the ion–dipole mechanism of the interaction[48]):



(XIV) .

The ODE has also been observed in the isoquinoline[46] and veratrol[47] series. The cause of the inertness of *o*-phenanthroline and benzo[1,2-*d* : 3,4-*d*′]di-imidazoles, which form complexes of types (XV) and (XVI) incapable of being aminated, is probably similar to the ODE:



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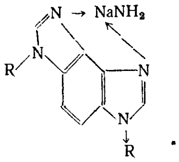

(XVI) .

The polarisability of the C=N bond. Bearing in mind the role of the >N → NaNH$_2$ coordination as the first stage of the Chichibabin reaction, when the latter is considered within the framework of the LCAO-MO theory, it is necessary to take into account the results of calculation not only for neutral molecules but also for heteroaromatic cations. Conversion into cations is accompanied by a sharp increase of the positive charge on the α-carbon atom (Table 3). The difference Δq_α^+ between the charges in the base and in the cation is then not the same for different heterocycles, being a minimum for pyridine and increasing on passing to its benzologues. Δq_α^+ is particularly large for the benzo- and naphtho-imidazole systems and also perimidine. The variation of Δq_α^+ on passing from one heterocyclic system to another may be attributed to the different polarisabilities of their C=N bonds in the course of the >N→NaNH$_2$ coordination (the importance of the polarisability factor in the Chichibabin reaction was first mentioned by Abramovitch et al.[49,50]). Evidently, the greater the value of Δq_α^+, the greater should be the ease, other conditions being equal, of the interaction of the heterocycle with the metal amide. Table 3 presents the Δq_α^+ calculated by the Hückel molecular orbital method for a series of heterocycles whose pK_a values lie in the region most favourable for the Chichibabin reaction. Also included are the values of $\Delta\delta_\alpha$ characterising the chemical shift of the α-CH proton in the ^{1}H NMR spectrum of the cation compared with the corresponding base. Overall, the variation of Δq_α^+ and $\Delta\delta_\alpha$ are the same.

Table 3. The effective positive charges q_2^+ and the chemical shift δ_2 of the protons of the α-carbon atom in certain heterocycles and their cations[27].

Compound	Neutral molecule		Cation		Δq_2^+	$\Delta\delta_2$, p.p.m.
	q_2^+	δ_2, p.p.m.	q_2^+	δ_2, p.p.m.		
Pyridine	+0.077	8.60	+0.241	8.98	+0.164	+0.38
Isoquinoline	+0.105	9.31	+0.329	10.07	+0.224	+0.76
Benzo[*f*]quinoline	+0.095	9.18	+0.276	9.95	+0.181	+0.77
Acridine*	+0.105	8.97	+0.288	10.15	+0.183	+1.18
Benzimidazole	+0.170	8.18	+0.443	9.61	+0.273	+1.43
Naphtho[1,2-*d*]imidazole	+0.152	8.15	+0.419	9.67	+0.267	+1,52
Perimidine	+0.256	7.41	+0.511	8.98	+0.255	+1.57

*Data for the γ-position.

On the basis of kinetic data, heterocycles can be arranged in the following series in terms of the ease with which they enter into the Chichibabin reaction: benzimidazole > isoquinoline > perimidine > benzo[*f*]quinoline > pyridine ≫ acridine[16]. If acridine is excluded (difficulty of γ-amination), this series agrees very closely with the variation of Δq_α^+, except for the fact that isoquinoline and perimidine change places. However, it is difficult to expect that a complex process such as the Chichibabin reaction should be ideally correlated in terms of a single electronic parameter. Apar from polarisability, the basicity of the compound, the positive charge on the α-carbon atom, the ease of aromatisation of the σ-complex, and possibly certain other factors play a role.

The possibility of a radical-anion stage in the Chichibabin reaction. The view that radical stages are possible in nucleophilic substitution reactions of aromatic compounds has become established in recent years[51–56]. It has also been shown in relation to the Chichibabin reaction that it is sensitive to the action of inhibitors of free radical processes[16]. It has been

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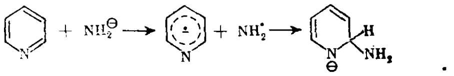
§ The claim[45] that only 9-aminoacridine is formed under these conditions in 72% yield was not confirmed[44].

suggested that a one-electron transfer stage probably precedes the formation of the σ-complex and takes place immediately after the sorption of the heterocycle on the $NaNH_2$ surface:

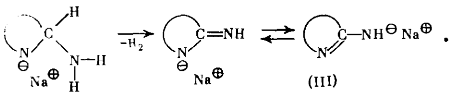


(XVII)

It must be emphasised that the introduction of the electron transfer stage does not conflict with the other considerations concerning the addition mechanism stated above and merely refines them, making it possible to explain many additional facts. In particular, certain compounds containing electron-accepting groups (NO_2, Ar–N=N, etc.) are not aminated, despite their satisfactory basicity and the large value of q_α^+. Presumably these substituents decrease with spin density in the 2-position of the radical-anion (XVII) and thereby prevent the recombination of radicals with formation of the σ-complex. On the whole, the problem of the intermediate formation of radical-anions in the Chichibabin reaction requires further study.

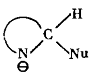
(b) The Elimination Stage

There are two main points of view concerning the mechanism of the aromatisation of the σ-complex in the Chichibabin reaction. The first, illustrated in Scheme (1), involves the loss of sodium hydride by the σ-complex. According to the Scheme (2), proposed in an early study by Bergstrom[11-15], the σ-complex is stabilised by the direct loss of an H_2 molecule as a result of the elimination of a proton from the NH_2 group and a hydride ion from the tetrahedral carbon atom:



(I) (III) (2)

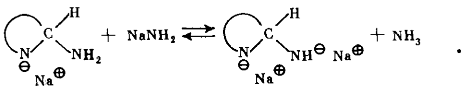
Scheme (2) is supported, in particular, by the fact that the reactions of nitrogen-containing heterocycles with anionic nucleophiles take place particularly readily when the nucleophile contains at least one hydrogen atom capable of being protonated. These include the $\overset{\ominus}{NH_2}$, $\overset{\ominus}{OH}$, and $\overset{\ominus}{NHR}$ anions. The σ-complexes (XVIII, a–c) corresponding to them



(XVIII) (a) Nu = NH_2; (b) Nu = OH;
(c) Nu = NHR;
(d) Nu = NR_2; (e) Nu = OR .

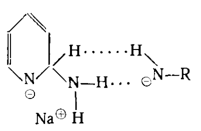
may be aromatised as a result of the loss of an H_2 molecule without preliminary elimination of sodium hydride. When the anions of secondary amines or metal alkoxides, whose σ-complexes (XVIII, d and e) cannot be stabilised in this way, are used as the nucleophiles, it is as a rule impossible to achieve the corresponding substitution reactions.

Direct elimination of hydrogen from the σ-complex is also likely to be a simplification. Clearly the mixture must contain the corresponding hydride ion and proton acceptors for this to occur. It has been suggested[12,57] that a hydride ion is eliminated from the dianionic σ-complex (XIX), formed as a result of an acid–base interaction, and not from the σ-complex (I):



(I) (XIX)

The possibility of the formation of such complexes is indirectly confirmed by ^{1}H NMR data[25,26] and by the finding that in liquid ammonia the amination reaction proceeds at an appreciable rate only in the presence of an excess of the metal amide[12]. In terms of this interpretation of the aromatisation stage, the evolution of hydrogen should occur as a result of the elimination of the hydride ion from the complex (XIX) with the aid of an ammonia molecule, i.e. in fact we are dealing here with bifunctional catalysis via a transition stage (XX). The decisive evidence in support of bifunctional catalysis is apparently the observation of the catalytic effect on the Chichibabin reaction of added sodium salts of amines and the presence of an autocatalytic section on the kinetic curves representing the variation of the rate of evolution of H_2.[16] Despite the presence in the mixture of an excess of more basic amide ions, the salts (III) catalyse the reaction, which shows that, in the transition complex (XX)



(XX)

(a), R=H, (b), R=heteroaryl.

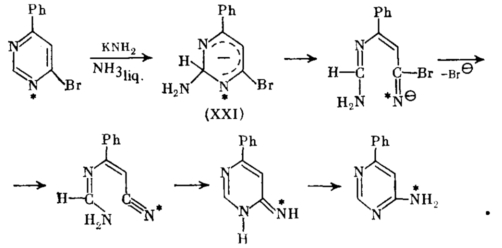
the hydride ion is eliminated with greater difficulty than the proton, i.e. not only the elimination of the proton but also the elimination of the hydride ion is catalysed. This implies that the transition state in the elimination stage is close to the σ-complex (XIX) and not the Ziegler adduct (I), as has been believed hitherto.

The hydride ion may be eliminated from the σ-complex also with the aid of a molecule of the initial compound, which entails the formation of dihydro-derivatives[16].

The foregoing considerations refer to heterogeneous amination. Successful amination in liquid ammonia takes place only in the presence of oxidants (KNO_3 is usually employed[11-15]), which convert the intermediate adduct (I) into an amine.

The behaviour of halogeno-derivatives of *N*-heterocycles in relation to metal amides. There has not been a single example in the literature hitherto of successful amination of halogenated *N*-heterocycles by the Chichibabin reaction, although such attempts have been made[4]. It is well known that halogeno-derivatives of heterocycles interact with metal amides, the halogen atom being substituted by an amino-group either via the S_N2Ar mechanism[5,6] or via the heteroaryne mechanism[58]. These reactions are usually carried out in liquid ammonia.

The so called *ANRORC* mechanism, proposed recently by Dutch chemists, throws some light on the characteristics of the behaviour of halogenated *N*-heterocycles in the Chichibabin reaction[59,60]. This mechanism is particularly characteristic of compounds of the pyrimidine series, for example:

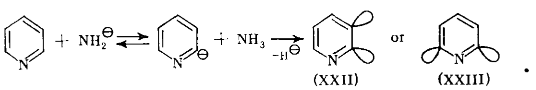


The reaction begins with the addition of an NH_2 ion to $C_{(2)}$ atom, without a halogen. The resulting σ-complexes of type (XXI) have been recently detected[61,62]. An important feature of these complexes is that they are stabilised by the elimination of a bromide ion with synchronous or stage-by-stage recyclisation and not by the loss of an $H^\ominus$ ion, which would constitute the Chichibabin reaction. As a result, the N atoms of the amide ion and the heterocycle change places. The *ANRORC* mechanism usually competes with the S_N2Ar or *EA* mechanism[59,60].

Yet another possible cause of the inability of halogenated heterocycles to be aminated by the Chichibabin reaction is the fact that their radical-anions (the possible reaction intermediates) are frequently fragmented with the loss of a halide ion[63]. Nevertheless it appears of interest to investigate the behaviour of halogenated *N*-heterocycles in relation to $NaNH_2$ in an aprotic medium. This applies particularly to compounds containing a relatively immobile halogen (for example, 3-bromopyridine).

(c) The "Elimination-Addition" Mechanism

The *EA* mechanism proposed for the Chichibabin reaction in 1963,[64,65] involving the intermediate formation of heteroarynes of type (XXII) or (XXIII), has been vigorously criticised[4,5,66,67]:

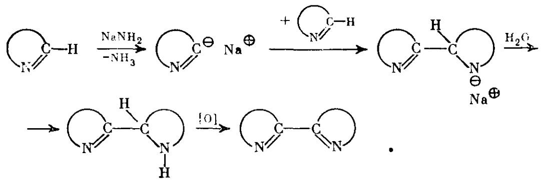


The following main evidence has been put forward:

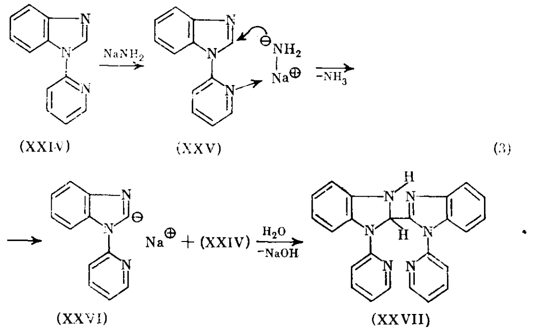
1. The absence of a kinetic isotope effect in the amination of a mixture of [2-D]pyridine and [3-D]pyridine.
2. The preferential amination of 3-substituted pyridines in the 2-position.
3. Successful amination of heterocycles which cannot form an aryne (azoles, acridine, isoquinoline). The amination of 2,5-disubstituted pyridines[68] also cannot involve the intermediate formation of 2,3- or 2,6-dihydropyridine.
4. According to calculations by the extended Hückel method, the arynes (XXII) and (XXIII) are much less stable than 3,4-dehydropyridines[69], which has been confirmed by data for the reactivities of 2- and 3-halogenopyridines[58].

2. SIDE REACTIONS

The most typical side reaction in the Chichibabin reaction amination of heterocycles is their dimerisation involving the α- or γ-positions. The formation of dimers with aromatic or hydrogenated structures has been observed for pyridine[1,3,7], quinoline[70], acridine[44], quinoxaline[71], and *N*-substituted benzimidazoles[27,38,46,72]. The yield of the dimer, which sometimes reaches 60%, depends strongly on the nature of the heterocycle and the solvent. The dimerisations mechanism is still not entirely clear. In principle, the reaction may reduce to the metallation of the α-CH bond with subsequent nucleophilic addition of the carbanion to the C=N bond of a second molecule[27]:



Another pathway involves the dimerisation of the intermediate radical-anion of type (XVII). According to the authors of the present review, both dimerisation pathways occur in different cases. For example, bearing in mind the ease of the polarographic reduction of acridine[73], the formation of 9,9′-biacridanyl (XIII) almost undoubtedly proceeds via a radical-anion mechanism. On the other hand, the formation of the dimer (XXVII) in 51% yield in xylene and in 10% yield in dimethylaniline when 1-α-pyridylbenzimidazole reacts with $NaNH_2$ probably involves the stage where the organosodium compound (XXVI) is formed, which may be favoured by intramolecular cooperation via type (XXV) coordination (such cooperative effects in the metallation of aromatic compounds have been described by, for example, Houghton[74] and Slocum and Stonemach[75]):

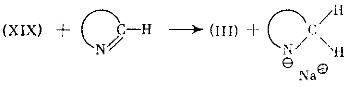


(3)

Scheme (3) is supported by the fact that 1-methyl-2-sodiobenzimidazole reacts with 1-methylbenzimidazole under the conditions of the Chichibabin reaction, giving rise to a high yield of 2,3-dihydro-1,1′-dimethyl-2,2′-bibenzimidazolyl[27]. It is noteworthy that the formation of organometallic compounds in the Chichibabin reaction should be accompanied by the evolution of gaseous ammonia. The presence of the latter in the gaseous reaction product does indeed range from 10 to 50%.[16,17] However, the main pathway leading to the formation of NH_3 is apparently the formation of the σ-complex (XIX) from the σ-complex (I). Thus up to 50% of NH_2 is evolved in the amination of 1-methylperimidine, although a dimer is not formed in the reaction at all[16].

The influence of solvents on dimerisation is indicated by the following facts. In the case of 1-alkylbenzimidazoles the formation of dimers in appreciable amounts (7–12%) is observed only in amination in dimethoxyethane or in the absence of a solvent. The amination of pyridine in hexamethylphosphoramide results in the formation of 4,4′-bipyridyl in 20% yield[7], the carbon atoms with the maximum spin density in the pyridine radical-anions being involved in the reaction[76].

The second in importance side reaction in the Chichibabin amination of heterocycles is the hydrogenation of their C=N bond, which leads to the formation of the corresponding dihydro-derivatives (XXVIII), sometimes in yields up to 25%. This reaction has been observed for phenanthridine[57], Schiff bases[20,21,77], and 1-methylperimidine. The mechanism probably involves the transfer of a hydride ion from the σ-complex (I) or, what is more likely, from the dianionic σ-complex (XIX), to the readily reduced C=N bond of the initial compound:



(XXVIII)

Other side reactions are specific to various compounds and will be considered in Section III.

3. THE INFLUENCE OF SOLVENTS

Unfortunately there are so far no quantitative data for the influence of solvents on the Chichibabin reaction. Taking into account the high polarity of the σ-complex, the ease of its formation should presumably depend on the solvating capacity and the dielectric constant of the solvent. Indeed in liquid ammonia, a solvent with proton-accepting and proton-donating activities which also has a very high dielectric constant ($\epsilon = 25.4$), the σ-complexes of many heterocycles with metal amides are formed even at $-40°$.[25,26] On the other hand, in inert solvents such as aromatic hydrocarbons ($\epsilon = 2-2.5$) σ-complexes are formed at 70–90°C and even higher temperatures. Dimethylaniline, dimethoxyethane, tetrahydrofuran, ($\epsilon = 7-7.5$), and other related solvents occupy an intermediate position between liquid ammonia and hydrocarbons. Amination in dimethylaniline takes place as a rule at a lower temperature and faster than in xylene or toluene although in isolated instances side products are formed in large amounts[37]. Reports have been published recently about the successful use of tetrahydrofuran and dimethoxyethane as solvents[27,57]. Thus phenanthridine is aminated in tetrahydrofuran even at room temperature[57].

Amination without a solvent has been described for 1-alkylbenzimidazoles[27], pyrazine[78], pyridine[79], anabasine[80], *N*-methylanabasine, and nicotine[80], the yields of the amino-derivative in the last two cases being even higher than in the presence of a solvent.

III. INTERACTION OF NITROGEN-CONTAINING HETEROCYCLES WITH METAL AMIDES

All the heterocycles which have been made to undergo the Chichibabin reaction hitherto contained a pyridine nitrogen atom. The role of the latter consists in the activation of the ring with respect to nucleophilic substitution by analogy with the function of the nitro-group in aromatic compounds. Indeed the σ constants of the nitro- and aza-groups are extremely similar[81]. Heterocycles with a single nitrogen atom of the pyridine type are aminated most effectively: pyridine, quinoline, isoquinoline, phenanthridine, and benzoquinolines. When several aza-groups are introduced into the molecule, the situation becomes more complex and treatment with $NaNH_2$ can lead to either amination (naphthyridines, pyrazines) or to side reactions (quinoxaline, triazine). Systems with excess π electrons, containing only a pyrrole nitrogen atom (indoles, indolizine, etc.), do not undergo the Chichibabin reaction. The only heterocycle with excess π electrons, which it has been possible to introduce into the reaction is perimidine, but its molecule contains a pyridine nitrogen atom in addition to a pyrrole nitrogen atom.

Azoles, another class of compounds with heteroatoms of both types, behave in different ways in relation to metal amides. Non-condensed azoles (imidazole, pyrazole) are usually not aminated, although there are exceptions (thiazole). The situation changes in benzazoles and naphthazoles as a result of the depletion of the heterocyclic ring in electrons and the compounds show a tendency towards amination (benzimidazole, naphthimidazoles), although this is not always the case (indazole and benzoselenazole are not aminated).

The pre-rearrangement of the N=CH group by $NaNH_2$ in a manner favouring amination is apparently so pronounced that the group is sometimes aminated even when it is not incorporated in a ring. Thus Schiff bases have been made to undergo the Chichibabin reaction[20,21,77].

The foregoing may create the impression that the presence of a pyridine nitrogen atom is a necessary condition for amination. However, such a claim must be approached with caution. In an early study Sachs showed that under severe conditions even compounds such as naphthalene, naphthylamines, and naphtholes may be aminated by sodium amide[82], hydrogen being evolved in the reaction (i.e. the latter proceeds as nucleophilic substitution). Later other non-heterocyclic compounds (mesobenzanthrone[83,84] and nitrobenzene[85]) were aminated, although the yields of amines in these instances are low. Evidently the problem of the possible amination of heterocycles without an aza-group requires further study.

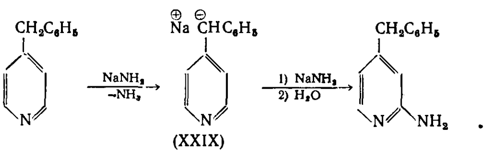
1. AZINES

(a) Pyridines

Pyridine and its 2- and 4-substituted derivatives. Despite the widely held view, pyridine is one of the most slowly aminated heterocycles. In contrast to diazines, quinoline, and isoquinoline, it does not, for example, react with KNH_2 in liquid ammonia even after prolonged treatment[25]. The amination of pyridine requires heating for many hours at 105–130°C (the yield of 2-aminopyridine is 70–85%).[1,79,86-88] Small amounts of bipyridyls, 2,2′-dipyridylamine, and 4-aminopyridine are formed as side products[1,3]. 2,6-Diaminopyridine may be obtained in 55% yield at 170–180°C [1] and 2,4,6-triaminopyridine may be formed in a low yield at 200°C and in the presence of a large excess of $NaNH_2$.[42] The relative difficulty of aminating pyridine can be accounted for by the comparatively low positive charge on the α-carbon atom and also by the low polarisability of the C=N bond (Tables 1 and 3).

2-Alkylpyridines ($R = CH_3$ [1,86-91] or n-C_3H_7 [3]) are aminated in the free α-position; if the latter is occupied, γ-amination takes place to a small extent[43]. 2,4,6-Trisubstituted pyridines do not enter into the Chichibabin reaction[1] and 2-t-butylpyridine is not aminated even under severe conditions[92]. The bulky t-butyl group apparently prevents, owing to steric considerations, the sorption of the compound on the $NaNH_2$ surface. The phenyl group has less stringent requirements and 2-phenylpyridine yields 6-amino-2-phenylpyridine (in dimethylaniline at 130–140°C) in 87% yield together with a small amount of the 4,6-diamino-derivative[93,94].

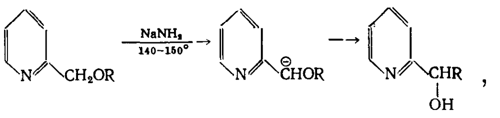
4-Alkylpyridines (R = CH_3,[95] C_2H_5,[96] n-C_3H_7,[97] or n-C_5H_{11}[98]) are converted into 2-amino-derivatives in 60 to 76% yields; 2,6-diamino-derivatives are not then formed. The high yields of amines in the amination of α- and γ-picolines show that in aprotic solvents the CH_3 group does not ionise (such ionisation takes place only in liquid ammonia[99]). On the other hand, 4-benzylpyridine initially forms the carbonium ion (XXIX), which is aminated with difficulty[98]:



(XXIX)

The difficulty of amination owing to analogous ionisation increases also for amino- and hydroxy-pyridines. Thus γ-pyridone is aminated only at 250°C in liquid paraffin, forming 2,6-diamino-4-hydroxypyridine in 69–75% yield[100]. α-Pyridone is aminated to 2-amino-6-hydroxypyridine[88]. The reaction of 2-aminopyridine with $NaNH_2$ at 120–130°C is accompanied by vigorous evolution of ammonia and the resulting salt (III) is aminated further to 2,6-diaminopyridine only at 160–180°C (in 71–79% yield)[41,87]. 4-Aminopyridine could not be introduced into the Chichibabin reaction[41]. The data for the amination of 3-aminopyridines are contradictory[41,101].

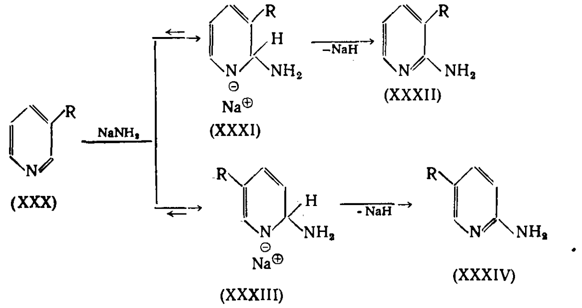
In certain cases the treatment of pyridine with $NaNH_2$ is accompanied by rearrangements or the elimination of substituents. Thus 2- and 4-alkoxymethylpyridines undergo the Wittig rearrangement[102]:



where R = C_2H_5, $C_6H_5CH_2$, etc. On treatment with $NaNH_2$, 2-dimethylaminopyridine gives a 30% yield of 2,6-diaminopyridine, the dimethylamino-group being substituted initially[41,103]. 4-Dimethylaminopyridine is aminated in the 2-position without the elimination of the substituent, but 4-diethylaminopyridine undergoes dealkylation, resulting in the formation of the sodium salt of 4-ethylaminopyridine, which is inert in relation to further treatment with $NaNH_2$.[41]

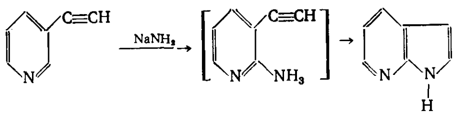
Pyridine-4-carboxylic acid and its amide are converted into 2,6-diaminopyridine on amination[104].

Substituted pyridines. One of the interesting features of the Chichibabin reaction is the preferential amination of 3-substituted pyridines (XXX) in the 2-position (Table 4).



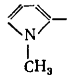
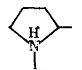
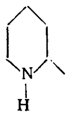
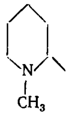
(XXX) (XXXI) (XXXII) (XXXIII) (XXXIV)

As expected, 3-alkyl-groups deactivate the ring with respect to the amide ion, but the 2-position is deactivated more than the 2-position[5,50]. This feature of the amination reaction has been successfully used in the synthesis of 7-azaindole from 3-ethynylpyridine[111]:



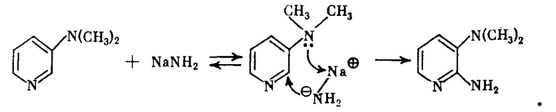
When compounds with bulky groups in the 3-position are aminated, the yield of the 6-amino-derivatives becomes equal to that of the 2-isomer or even exceeds it (Table 4).

Table 4. Amination of 3-substituted pyridines (XXX).

R	Reaction products (the ratios of the isomers are indicated in brackets)	Overall yield, %	References
CH_3	(XXXII) + (XXXIV) (10,5:1)	50	49,50,105,106
CH_3	2,6-diamino-3-methyl-pyridine	4	107
C_2H_5	(XXXII) + (XXXIV) (3.5:1)	64	108,109
н-C_4H_9	(XXXII) + (XXXIV) (4:1)	50	110
C≡CH	7-azaindole	54	111
$NHCH_3$	(XXXII)	—	112
OH	2,6-diaminopyridine	55	113
$N(CH_3)_2$	(XXXII)	62	41
COOH	2,6-diaminopyridine	12	114
$CONH_2$	2,6-diaminopyridine	44	114
$CONH_2$	(XXXII)	25	115
	(XXXII) + (XXXIV) (7.3:10)	45	116
	(XXXII) + (XXXIV) (9:11)	60—68	117—120
	(XXXII) + (XXXIV) (1:20)	40	117,121—123
	(XXXII) + (XXXIV) (1:1)	46	117,122,124

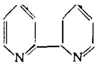
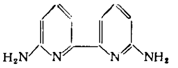
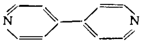
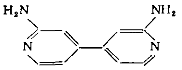
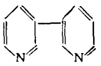
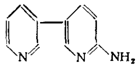
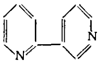
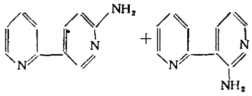
An analogous directing effect obtains in the interaction of 3-alkylpyridines with methyl-[125] and phenyl-lithium[126,127]. The nature of this phenomenon has been frequently discussed. No clear correspondence has been discovered between the position to which the nucleophile is directed and any reactivity index[128], which is not surprising, since steric and solvation effects and the possible interaction of the 3-substituent and the nucleophile in the transition state are ignored in calculations of this kind. The preferential formation of the 2-amino-derivative is believed to be associated with the fact that the corresponding σ-complex (XXXI) loses a hydride ion faster than the σ-complex (XXXIII).[5,50,126] This explanation is satisfactory if the rate of reaction is limited by the aromatisation stage. However, as already stated, a kinetic isotope effect has not been observed in the Chichibabin reaction[66].

The most attractive explanation is the hypothesis that the nucleophile is directed to the 2-position by London forces or the ion–dipole interaction of the nucleophile with the 3-substituent in the transition complex[5,50,129]. Such interaction should be particularly appreciable for 3-dimethylaminopyridine. Indeed, this compound is aminated exclusively in the 2-position[41]:



Other pyridines. The few studies on the amination of bipyridyls have shown that the latter react with $NaNH_2$ with much difficulty, forming amino-derivatives in low yields. Data for the amination of bipyridyls and disubstituted pyridines are presented in Table 5.

Table 5. Amination of disubstituted pyridines and bipyridyls.

Compound	Reaction product	Yield, %	References
2,5-$Me_2C_5H_3N$	2-amino-3,6-dimethylpyridine	32	130
3,5-$Me_2C_5H_3N$	2-amino-3,5-dimethylpyridine	20	130
2,6-$Me_2C_5H_3N$	4-amino-2,6-dimethylpyridine	6	43
2-Me-5-EtC_5H_3N	2-amino-3-ethyl-6-methylpyridine	70	68,96,131
2-Me-5-n-PrC_5H_3N	2-amino-3-n-propyl-6-methylpyridine	—	131
2-Me-4-HOC_5H_3N	2-amino-4-hydroxy-6-methylpyridine	—	132
3,4-$(HO)_2C_5H_3N$	2-amino-3,4-dihydroxypyridine	40	133
		—	134*
		—	96*
		—	135*
		—	136*

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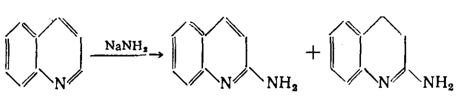
*There is no information about the yields.

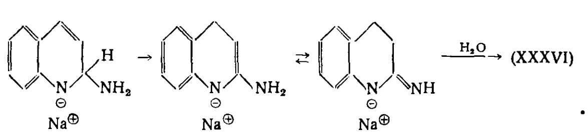
(b) Condensed Systems Containing a Pyridine Ring

In aprotic solvents quinoline is ineffectively aminated: the yield of 2-aminoquinoline (XXXV), which is difficult to purify, does not exceed 32% in toluene[1,70] and xylene[79]. In dimethylaniline the yield of (XXXV) falls to 7% and the main product becomes, somewhat unexpectedly, 2-amino-3,4-dihydroquinoline (XXXVI) (yield 24%):[137]



(XXXV) (XXXVI)

The formation of (XXXVI) can be represented schematically as follows:



This reaction occurs also for certain quinoline derivatives[138,139]. The highest yield of 2-aminoquinoline (53–69%) may be reached by amination by barium or potassium amides in liquid ammonia[13]: in the latter case 4-aminoquinoline is also formed in 10% yield.

As already mentioned, quinoline forms two σ-complexes in liquid ammonia—the 2-amino-1,2-dihydroquinolinide anion (VIII) and the 4-amino-1,4-dihydroquinolinide anion (IX).[26] Despite the fact that the latter is thermodynamically more stable, quinoline is nevertheless aminated mainly in the 2-position. A possible explanation of this finding is that (VIII) is aromatised faster (in liquid ammonia, to which the above considerations refer, the aromatisation stage is undoubtedly rate-limiting).

The results of the amination of various quinoline derivatives are presented in Table 6, which shows, in particular, that quinolines are much more readily aminated in the γ-position than pyridines.

2- and 4-Methylquinolines are not aminated in liquid ammonia owing to the ionisation of the methyl groups[14,142]. However, 4-methylquinoline is aminated in dimethylaniline (Table 6). In contrast to pyridine derivatives, quinolinecarboxylic acids and their amides are aminated without the elimination of the substituent. Hydroxy- and amino-quinolines are not aminated even under severe conditions[14].

Table 6. Amination of monosubstituted quinolines.

Substituent in initial compound	Substituents in reaction product	Yield, %	References
2-COOH	4-amino-2-carboxy-	81	14
2-C_6H_5	4-amino-2-phenyl-	91	15
2-OCH_3	2-amino-	51	14
2-SO_3H	2-amino-	74	14
2-$NHCH_3$	2-amino-	15	140
2-$N(CH_3)_2$	2-amino-	—	140
4-CH_3	2-amino-4-methyl-	46	3
4-COOH	2-amino-4-carboxy-	70	14
4-$CONH_2$	2-amino-4-carbamoyl-	54	141
6-CH_3	2-amino-6-methyl-	17	14
6-COOH	2-amino-6-carboxy-	60	14
6-C_6H_5	2-amino-6-phenyl-	86	15
6-$N(CH_3)_2$	2-amino-6-dimethylamino-	34	14
6-OCH_3	2-amino-6-methoxy-	27	14
6-SO_3H	2-amino-6-sulpho-	40	14
7-CH_3	2-amino-3,4-dihydro-7-methyl-	4,3	139
8-CH_3	2-amino-8-methyl-*	35	14,138
8-C_6H_5	2-amino-8-phenyl-	88	15
8-OC_2H_5	2-amino-8-ethoxy-	76	14

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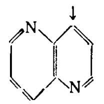
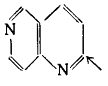
*2-Amino-8-methyl-3,4-dihydroquinoline was also isolated (1%).[128]

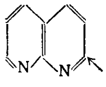
Isoquinoline is one of the most readily aminated heterocycles; the amino-group enters exclusively the 1-position. The yield of 1-aminoisoquinoline is quantitative in dimethylaniline[44], 87% in liquid ammonia[12,13], and 38% in toluene[143]. Isoquinoline-4-carboxylic acid[144], 5,6,7,8-tetrahydroisoquinoline[145], and 7-methoxyisoquinoline[146] are also satisfactorily aminated.

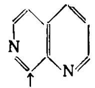
5,6- and 7,8-benzoquinolines give rise to high yields of 2-amino-derivatives both in liquid ammonia[15] and in dimethylaniline[147]. Phenanthridine is readily aminated in the 6-position in dimethylaniline[148,149], xylene[148], tetrahydrofuran[57], and liquid ammonia[42], but the amount of hydrogen evolved is less than the theoretical amount, which can be explained by the formation of 5,6-dihydrophenanthridine as a side product (yield 20%).[57] The amination of acridine was discussed above (Section II, 1a).

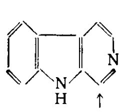
The amination of several compounds in which the pyridine ring is condensed to a further heteroatomic system has been described. These include the naphthyridines (XXXVII)–(XL),[150,151] β-carboline (XLI),[152] imidazo[4,5-*c*]-pyridine (XLII),[153] pyrido[4,5-*b*]-pyridazine (XLIII),[154] and imidazo[4,5-*f*]quinoline (XLIV) [147] (the arrow indicates the site where the amino-group enters):

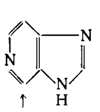

(XXXVII)

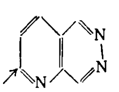

(XXXVIII)

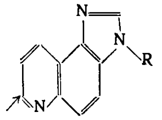

(XXXIX)


(XL)

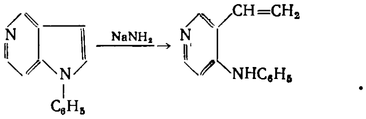

(XLI)


(XLII)


(XLIII)


(XLIV)

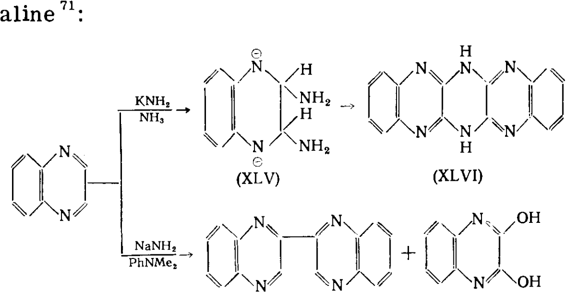
It was not possible to aminate 7-azaindolines[41], 7-azaindole[155], 1-methylimidazo[4,5-*b*]pyridine[156,157], 1-benzyl-4-azaindole, and 1-phenyl-5-azaindole[41]. It is of interest that the last compound is converted into 4-phenylamino-3-vinylpyridine on treatment with sodium amide[41], i.e. formally two-electron reductive cleavage of the C–N ring bond takes place:



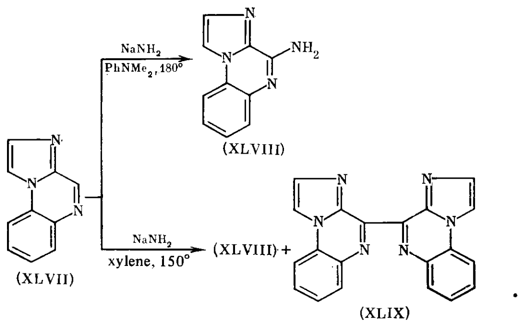
(c) Diazines and Triazines

Pyridazine does not undergo the Chichibabin reaction[154], although it does form the σ-complex (XVI) in liquid ammonia[25]. There has been only one report of the amination of pyrimidine derivatives: when 4-methylpyrimidine was treated with $NaNH_2$ in decalin, 2-amino-4-methyl- and 2,6-diamino-4-methyl-pyrimidines were isolated (the yields are not indicated)[158]. Pyrazine is aminated by sodium amide without a solvent, forming 2-aminopyrazine in a low yield (8–17%);[78] the available data on the amination of pyrazine in liquid ammonia are contradictory[159,160]. Amino-derivatives of 2,5-dimethylpyrazine are formed in 10% yield in xylene[161] and 35% yield in dimethylaniline[162]. 2,5-Di-s-butylpyrazine has been converted into an amine in 60–65% yield[163].

The reactions of quinoxaline with alkali amides take place in a complex manner and without the evolution of hydrogen. In liquid ammonia the only identified product of the reaction with two equivalents of potassium amide was fluorubine (XLVI).[160] It is apparently formed as a result of the reaction of the σ-complex (XLV) [164] with a molecule of the initial compound. In dimethylaniline the reaction of quinoxaline with sodium amide at 210–225°C gives rise to 2,2′-biquinoxalinyl and 2,3-dihydroxyquinoxaline[71]:



The only quinoxaline derivatives aminated under the conditions of the Chichibabin reaction proved to be imidazo[1,2-*a*]quinoxaline (XLVII): the amine (XLVIII) was isolated in 44% yield in dimethylaniline, while in xylene its yield fell to 11% and the main product became the dimer (XLIX):[72]

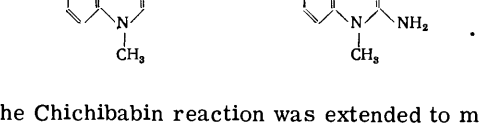


Quinazoline is aminated to 4-aminoquinazoline in dimethylaniline[33]. 4-Mercaptoquinazoline and 4-mercapto-6,7-benzoquinazoline are aminated with elimination of the mercapto-group and the formation of 2,4-diamino-derivatives[165]. Analogous results were observed also for 5,6-benzoquinazoline and its mercapto-derivatives[165].

Among triazines, the 1,3,5-isomer reacts with $NaNH_2$ and is cleaved to sodium cyanide in xylene at 160°C.[166] Pteridine, which is soluble in liquid ammonia, combines with ammonia covalently, but decompose when acted upon by KNH_2.[167]

2. IMIDAZOLE SYSTEMS

In 1951 Simonov and Uglov[2] demonstrated the possibility of the amination of the imidazole ring in the 2-position in relation to 5-methoxy-5-methylbenzimidazole:

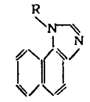
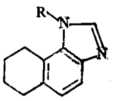
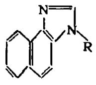
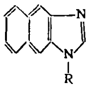
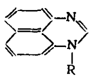
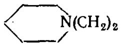
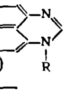


After this, the Chichibabin reaction was extended to many benzimidazole derivatives and a series of imidazole systems[4,8]. One should note that imidazoles with a free amino-group are not aminated, since they are converted into the *N*-anion, which is inert in relation to sodium amide.

The possibility of the amination of imidazole derivatives is determined mainly by three structural factors: (1) the nature of the ring condensed to the imidazole ring; (2) the structure of the substituent at the pyrrole nitrogen atom; (3) the influence of the substituents in the aromatic ring.

The nature of the ring condensed with the imidazole ring. Whereas *N*-derivatives of benzimidazole, the isomeric naphthimidazoles, and 6,7,8,9-tetrahydronaphtho[1,2-*d*]imidazole are readily aminated in the 2-position (Table 7), *N*-substituted imidazoles, 4,5-diphenylimidazoles, and 5,6,7,8-tetrahydrobenzimidazoles do not undergo the Chichibabin reaction[168]. Thus, successful amination of the imidazole ring requires that it should be condensed to an aromatic ring. The role of the latter probably consists in creating a fairly large positive charge on the α-carbon atom as a result of the delocalisation of the π electrons (Table 2). The inability of phenanthro[9,10-*d*]imidazole to be aminated can be accounted for by the low aromaticity of the central benzene ring[168].

Table 7. Amination of naphthimidazoles, permidines, and aceperimidines.

Compound	R	Yield of amine, %	References
	C_2H_5	45	169
	CH_3	45	169
	CH_3 $C_6H_5CH_2$	75 75	169,170 171
	CH_3 $C_6H_5CH_2$	52 67	172 172
 (L)	CH_3 C_2H_5 n-C_3H_7 CH_3OCH_2 $C_6H_5CH_2$  $CH_2CH_2CH_2N(CH_3)_2$ C_6H_5	90 (75)* 90 70 30 (75)* 75 52 41 100	40 40 40 40 40 173 174 174
 (LI)	CH_3 C_2H_5	30 (75)* 25 (68)*	40 40

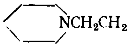
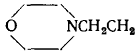
*The yield varies as a function of the solvent.

It is of interest that imidazoles which are not aminated readily undergo the azo-coupling reaction in an alkaline medium involving the μ-carbon atom, while imidazoles capable of being aminated do not react with diazonium salts; this difference served at one time as a test for ability to be aminated. This finding clearly demonstrates the differences between the charges in the μ-positions of the two types of azoles. However, there are also exceptions. *N*-derivatives of imidazo[4,5-*b*] phenazine[39], imidazo[4,5-*b*]pyridine[156], and purine[27] are inert both to diazonium salts (high q_{α}^{+}) and sodium amide (low basicity).

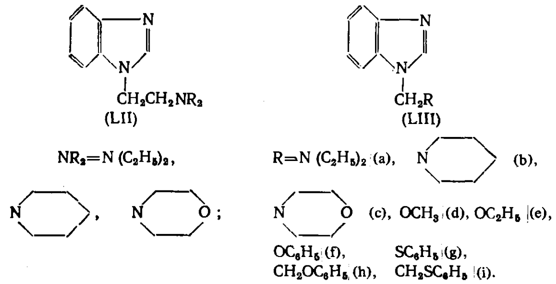
The influence of the *N*-substituent. The nature of the substituent at the nitrogen atom has a significant influence on the amination of imidazoles and in certain cases completely alters the mode of reaction.

Benzimidazoles containing straight-chain alkyl substituents are readily aminated at 105–120°C (Table 8). Secondary *N*-alkyl groups hinder the reaction only slightly[17]. 1-*t*-Butylbenzimidazole is aminated with a low yield[175].

Table 8. Amination of 1-substituted benzimidazoles.

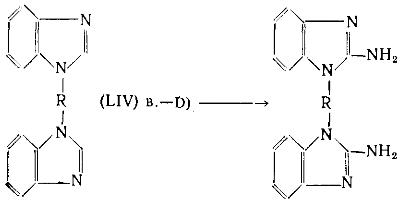
N-substituent	Yield of 2-amino-derivative, %	Refs.
CH_3	80	8,176
C_2H_5	85	26,168
n-C_3H_7	50	177
iso-C_3H_7	64	175,177
n-C_4H_9	55	177
t-C_4H_9	21	175
iso-C_9H_{19}	70	175
n-$C_{11}H_{23}$	64	175
$(C_2H_5)_2NCH_2CH_2$	50	178
	50	36
	40	36
cyclohexyl	70	37
$C_6H_5CH_2$	67	179
p-$CH_3C_6H_4CH_2$	72	180
p-iso-$C_3H_7C_6H_4CH_2$	63	180
2,5-$(CH_3)_2C_6H_3CH_2$	61	180
p-$HOC_6H_4CH_2$	29	46
p-$CH_3OC_6H_4CH_2$	61	46
$(C_6H_5)_2CH$	54	180
$(C_6H_5)(CH_3)CH$	34	181
α-Naphthylmethyl	15	181
C_6H_5	62	37
p-$CH_3C_6H_4$	47	27
p-$CH_3OC_6H_4$	74	39
o-$CH_3OC_6H_4$	82	39
p-$(CH_3)_2NC_6H_4$	71	39
2,4-$(CH_3O)_2C_6H_3$	66	46
2,5-$(CH_3O)_2C_6H_3$	60	46

1-β-Dialkylaminoethylbenzimidazoles (LII) are aminated with greater difficulty than 1-alkylbenzimidazoles. One of the possible explanations involves competing coordination of the nitrogen atom of the substituent to the sodium cation, which should hinder the reaction. Under the conditions of the Chichibabin reaction, 1-diethylaminomethylbenzimidazole (LIIIa) gives rise to benzimidazole and 1-piperidino- and 1-morpholino-methylbenzimidazoles (LIII, b and c) are converted into 1-aminomethylbenzimidazole[182]. Compounds (LIII, d–i) do not form amino-derivatives[36,182].



1-β-Pyridylethylbenzimidazoles do not react with $NaNH_2$ at 110–140°C, decomposing at a higher temperature with formation of benzimidazole and a tar [38].

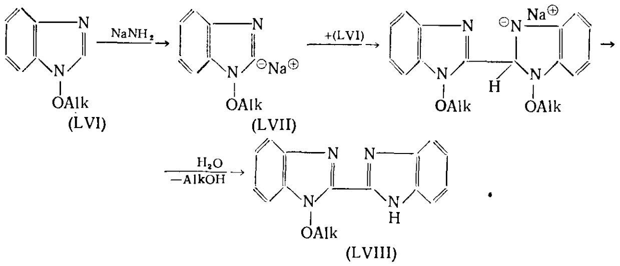
Depending on the length of the hydrocarbon chain, di-(1-benzimidazolyl)alkanes (LIV) behave in different ways in the Chichibabin reaction. Thus compounds (LIV, a, b, and f) are not aminated even at 180°C, while compounds (LIV, c–e) form the diamines (LV).[183] The reason for the difference between the reactivities is not altogether clear.



(LIV)
$R=CH_2$ (a), $(CH_2)_2$ (b), $(CH_2)_3$ (c), $(CH_2)_4$ (d), $(CH_2)_5$ (e), $CH_2C_6H_4CH_2$ (f);

(LV)
$R=(CH_2)_3$, $(CH_2)_4$, or $(CH_2)_5$.

The weakly basic 1-alkoxybenzimidazoles (LVI) are converted into the "dimers" (LVIII) when acted upon by sodium amide, probably via the intermediate carbanion (LVII):[184]



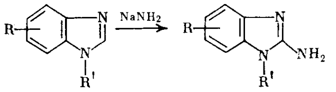
Thus the ease and mode of reaction of 1-substituted benzimidazoles with sodium amide greatly depend on the presence of a heteroatom in the substituent.

1-Benzylbenzimidazole and its derivatives with electron-donating substituents in the benzyl group are readily aminated (Table 8), with the exception of 1-*p*-hydroxybenzylbenzimidazole, which forms the less reactive *O*-anion, and 1-(3,4-dimethoxybenzyl)benzimidazole, which is converted into benzimidazole [46]. The formation of a dimer (7%) was observed in the amination of 1-*p*-methoxybenzylbenzimidazole [46]. Different 1-arylbenzimidazoles without electron-accepting substituents are also effectively aminated (Table 8). 1-γ-Pyridylbenzimidazole is inert with respect to $NaNH_2$, whereas 1-α-pyridylbenzimidazole is converted into the dimer (XXVII) under the same conditions[38] (Section II, 2).

The influence of substituents in the benzene ring of benzimidazole. When electron-accepting substituents (COOH, COOR, $CONH_2$, NO_2, N_3 PhN = N, F, Br, or Cl) are present in the benzene ring of benzimidazole, amination is impossible [8,39,185,186]. This is probably due to one of the following causes or their combination: (1) a decrease of the basicity of the nitrogen atom ($pK_a \leqslant 4.8$); the tendency of these groups to form non-aminated complexes with $NaNH_2$; (3) a change in the distribution of spin density in intermediate radical-anion which is unfavourable for amination.

Benzimidazoles with electron-donating groups in the benzene ring are readily aminated (Table 9), the substituents decreasing the rate of reaction in accordance with their electron-donating properties: 5,6-Me_2 < 5-MeO < 5-Me < 5-H.[17] 5-Hydroxy-, 5,6-dimethoxy-, and 5,6-methylenedioxy-benzimidazoles are not aminated [39,46] (Section I, 1a). 5-Amino-1-methylbenzimidazole is aminated under severe conditions [39].

Table 9. Amination of benzimidazoles substituted in the benzene ring



Substituents		Yield of 2-amino-derivative, %	Refs.
R	R′		
4-CH_3O	CH_3	57	39
5-CH_3	CH_3, $C_6H_5CH_2$	60—76	186
5-CH_3O	CH_3, C_2H_5, $C_6H_5CH_2$, $(C_2H_5)_2N(CH_2)_3$	55—63	2,39,176,18
5-C_2H_5O	CH_3, C_2H_5	55—60	185
5-$C_6H_5CH_2O$	CH_3	25	185
5-C_6H_5O	CH_3	70	185
5 CH_3S	CH_3	87	188
5-NH_2	CH_3	69	39
5-$N(CH_3)_2$	CH_3, C_2H_5	70—93	39
6-CH_3O	C_2H_5	52	39
7-CH_3O	$C_6H_5CH_2$	64	39
5,6-$(CH_3)_2$	CH_3, C_2H_5, C_6H_5, $C_6H_5CH_2$	38—91	189
4,7-$(CH_3O)_2$	$C_6H_5CH_2$	65	46

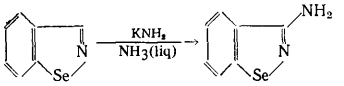
3. PERIMIDINES

Perimidines (L) are *peri*-isomeris of naphthimidazoles, but differ from the latter by the size of the heterocycle and a number of important physicochemical properties. Thus, together with a considerable deficiency of π electrons, a large excess of π electrons is also characteristic of perimidines [190], so that one may say that they are the only compounds with an excess of π electrons which enter into the Chichibabin reaction. The successful amination of perimidines is due to the strong polarisation of the C=N bond as a result of which a large positive charge is concentrated on the μ-carbon atom, where amination takes place, while a negative charge is created at the pyridine nitrogen atom (perimidines are much more basic than naphthimidazoles; see Table 2). Furthermore, the C=N bond in perimidines is highly polarisable (Table 3). *N*-Substituted aceperimidines (LI) undergo the Chichibabin reaction with much difficulty than perimidines. Data for the amination of perimidines and aceperimidines are presented in Table 7.

4. OTHER HETEROCYCLIC SYSTEMS

Thiazoles, selenazoles, and oxazoles. The Chichibabin reaction involving thiazoles and benzothiazoles proceeds in a complex manner and is of no practical importance. Sodium amide converts 4-methylthiazole into the 2-amino-derivative only after prolonged heating at 150°C.[191] Benzothiazole is aminated at 140°C but 2,2′-bibenzothiazolyl and bis-(2-aminophenyl) disulphide are formed together with 2-aminobenzothiazole [192].

When benzoselenazole was acted upon by $NaNH_2$, only bis-(2-aminophenyl) diselenide was isolated[193]. The amination of benzoisoselenazole with KNH_2 in liquid ammonia leads to the 3-amino-derivative, but its yield is low (36%):[194]



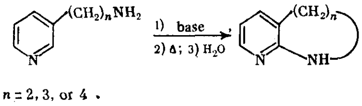
4-Methylselenazole[195] and isoxazoles[196] undergo ring opening without the formation of an amine.

Pyrazoles and indazoles. The positive charge on the α-carbon atoms of pyrazoles and indazoles are insufficient for amination. For this reason and also because of the lability of the nitrogen–nitrogen single bond, they are converted into ring-opening products and recyclisation products on being treated with methyl amides (see the relevant reviews[197,198]).

IV. REACTIONS RELATED TO THE CHICHIBABIN REACTION

Alkyl- and aryl-amination of heterocycles. The amination of nitrogen-containing heterocycles by organic derivatives of sodium amide is the closest analogue of the Chichibabin reaction. The possibility, in principle, of the phenylamination of pyridine in the 2-position by sodium anilide was demonstrated a long time ago[1]. However, owing to its low yields, the reaction is of no practical importance; furthermore, quinoline does not react with sodium anilide[22], while isoquinoline[13] and pyridine[199] do not react with sodium *N*-methylanilide. The alkylamination of heterocycles takes place successfully, but it has been little studied. Quinoline, acted upon by lithium methylamide, is known to form 2-methylaminoquinoline[200]. Alkali metal dialkylamides react only weakly with *N*-heterocycles or convert them into a tar[11,13,200].

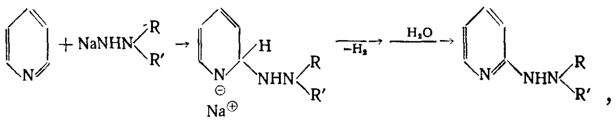
Bergstrom and coworkers achieved the alkylamination of pyridine and quinoline in the 2-position with the aid of aliphatic and alicyclic amines and the KNH_2-NaNH_2 eutectic in the presence of KNO_3.[201] The yield of reaction products reaches 60%. Kovacs and Vajda modified this method, having replaced the metal amide eutectic by metallic sodium[202–205]. Although it is natural to suppose that the aminating agent in these cases is sodium alkylamide, this is apparently not the case[204]. It has been suggested that the reaction proceeds via the intermediate formation of the pyridine radical-anion (as a result of electron transfer from sodium), which has been confirmed by the formation of 2,2′- and 4,4′-bipyridyls as side products and also by the available data on the mechanism of the interaction of sodium and pyridine[206]. An interesting variety of the reaction is intramolecular alkylamination of 3-ω-aminoalkylpyridines in the presence of strong bases (n-C_4H_9Li, Na, NaH, or $NaNH_2$) in dioxan or toluene[5,207,208]



$n = 2, 3,$ or 4 .

It must be emphasised that the reaction takes place in this case exclusively in the 2-position of the pyridine ring.

Hydrazination by metal hydrazides. The sodium salts of hydrazine, *N*-methylhydrazine, and *N*,*N*-dimethylhydrazine react very readily with pyridine, quinoline, 5,6- and 7,8-benzoquinolines, and their methyl derivatives with formation of the corresponding α-hydrazino-derivatives (LX):[209,210]



(LIX) (LX)

R, R′=H, or CH_3 .

The yields of products from pyridine and α-piccoline do not exceed 30%, those from quinoline do not exceed 45%, but in other cases the yields reach 70–80%.

In this reaction, which also proceeds with elimination of a hydride ion, a deeply coloured σ-complex (LIX) is formed initially[22,210], losing an H_2 molecule on heating and forming the corresponding hydrazine. A distinctive feature of the hydrazination reaction is the enhanced stability of the 1,4-adducts formed from pyridine and 2-methylquinoline: they are not aromatised even on heating[210]. It may be that their formation is the cause of the relatively low yield of 2-hydrazino-derivatives of pyridine and quinoline. Indeed, if the 4-position is occupied (γ-picoline, 4-methylquinoline, isoquinoline), α-hydrazination takes place with a satisfactory yield.

The adducts of acridine and phenanthradine with sodium hydrazide and dimethylhydrazide are anomalously stabilised. Instead of hydrogen, they split off on heating NH_3 and $(CH_3)_2NH$ molecules respectively, which results in the formation of 9-aminoacridine and 6-aminophenanthridine[22]. When quinazoline is acted upon by sodium hydrazide, hydrazination and amination take place simultaneously and 4-amino-2-hydrazinoquinazoline is formed[211]. Under these conditions, quinoxaline undergoes ring opening and pyrimidine undergoes ring contraction with formation of *o*-phenylenediamine and pyrazole respectively[211]. Yet another side reaction, which is observed, in particular, when pyridine is acted upon by sodium hydrazide, is the formation of hydrazo-compounds[210].

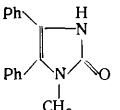
There is evidence for the possibility of direct hydrazination of benzoxazole and benzoselenazole[22]. Sodium phenylhydrazide could not be introduced into the reaction with heterocyclic compounds[209].

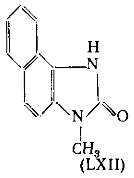
Hydroxylation of heterocycles. Direct hydroxylation of *N*-heterocycles is, as it were, the oxygen analogue of the Chichibabin reaction and is also accompanied by the evolution of hydrogen. The successful hydroxylation of both six- and five-membered heterocycles has now been achieved. α-Oxo-derivatives of pyridines[213–216], quinolines[215–218], benzoquinolines[218], isoquinoline[218], and phenanthridine were obtained by this method[219]. The hydroxylation of 1-substituted imidazoles and perimidines (Table 10), achieved for the first time by Pozharskii and coworkers[221], is of special preparative importance, because the *N*-monosubstituted imidazolidinones and perimidones, formed at the same time, are difficult to obtain by another procedure. It has been shown for compound (LXVI) and (LXVII) that, in the presence of two atoms active in relation to the nucleophile in the molecule of the *N*-heterocycle, both can be hydroxylated[183,220].

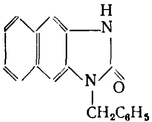
The hydroxylation can be carried out by fusing the heterocyclic compound with a large excess of anhydrous powdered alkali [KOH and, more rarely, NaOH and

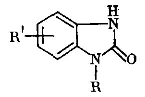
$Ba(OH)_2$]. Owing to the weak nucleophilic properties of the $OH^{\ominus}$ ion, the process proceeds at an extremely high temperature (usually above 200°C), but is nevertheless characterised by a surprisingly high selectivity and, as a rule, high yields (particularly for imidazoles and perimidines). The only known instance of γ-hydroxylation is the formation of acridinone in 40% yield on hydroxylation of acridine with KOH at 300°C.[44] The ease of hydroxylation depends mainly on the positive charge of the α-carbon atom (Table 2).[221] Thus 1-methyl-4,5-diphenylimidazole is hydroxylated at 370–400°C, while 1-substituted perimidines are hydroxylated at a temperature as low as 200°C.

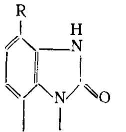
Table 10. Imidazolidinones and perimidones obtained by direct hydroxylation

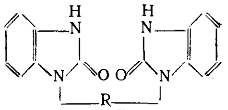

(LXI)

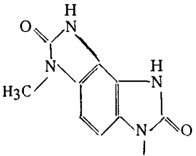

(LXII)

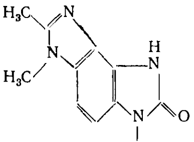

(LXIII)

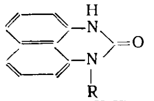

(LXIV)

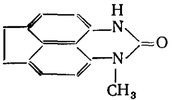

(LXV)

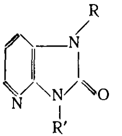

(LXVI)

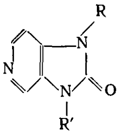

(LXVII)


(LXVIII)


(LXIX)


(LXX)

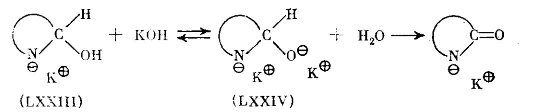

(LXXI)


(LXXII)

Compound	Substituents		Yield, %	References
	R	R′		
(LXI)	—	—	30	221
(LXII)	—	—	90	221
(LXIII)	—	—	80	222
(LXIV)	CH_3	H	90	221
(LXIV)	iso-C_3H_7	H	23	223
(LXIV)	n-C_9H_{19}	H	75	223
(LXIV)	$C_6H_5CH_2$	H	90	221
(LXIV)	C_6H_5	H	20	221
(LXIV)	*p*-$CH_3OC_6H_4$	H	70	221
(LXIV)	CH_3OCH_2	H	80	221
(LXIV)	CH_3	5-CH_3O	85	221
(LXIV)	$C_6H_5CH_2$	5,6-$(CH_3)_2$	85	221
(LXV)	H	—	58	224
(LXV)	$(C_2H_5)_2N$	—	33	224
(LXVI)	$(CH_2)_3$	—	50	183
(LXVI)	$(CH_2)_4$	—	81	183
(LXVI)	$(CH_2)_5$	—	91	183
(LXVII)	—	—	35	220
(LXVIII)	—	—	46	220
(LXIX)	CH_3	—	90	221
(LXIX)	C_2H_5	—	87	221
(LXIX)	CH_3OCH_2	—	82	221
(LXIX)	$(C_2H_5)_2NCH_2CH_2$	—	30	173
(LXX)	—	—	81	221
(LXXI)	CH_3	H	70	225
(LXXI)	H	CH_3	98	225
(LXXI)	H	$C_6H_5CH_2$	65	225
(LXXII)	CH_3	H	27	225
(I XXII)	H	CH_3	44	225

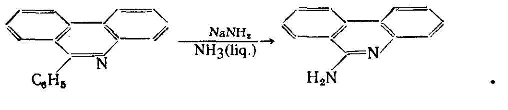
Much less is known about the side reactions in the hydroxylation process than for the Chichibabin reaction. Thus, on being fused with KOH, 1-phenylbenzimidazole gives rise to 1,1′-diphenyl-2,2′-bibenzimidazolyl together with 1-phenylbenzimidazolidinone[221]. On treatment with KOH, 1-methoxymethyl-, 1-isopropyl-, and 1-t-butylbenzimidazoles are converted into benzimidazole and other decomposition products, i.e. the elimination of the *N*-substituent is observed.

The hydroxylation mechanism probably resembles the mechanism of the Chichibabin reaction, although it has not been specially studied. We have reason to believe that the dianionic σ-complex (LXXIV) is formed as an intermediate: before the evolution of hydrogen, water is usually distilled off, which displaces the equilibrium (LXXIII) ⇌ (LXXIV) to the right:



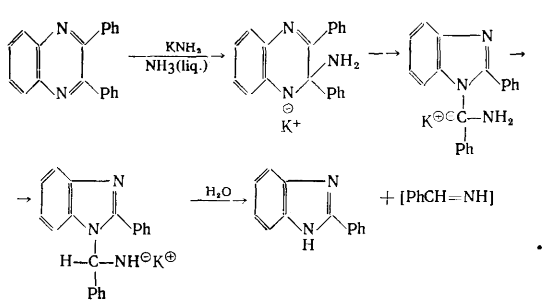
Direct alkoxylation of *N*-heterocycles by metal alkoxides could not be achieved[221].

Amination and hydroxylation with elimination of a carbanion. In our discussion of the Chichibabin reaction involving pyridine and quinolines we quoted a number of reactions in which the leaving groups were NMe_2, SO_3H, a halogen, etc. and not a hydride ion. However, all the groups are readily eliminated. In this respect the reactions of *N*-heterocycle derivatives, in which their amination by metal amide is accompanied by the elimination of a hydrocarbon substituent, are much closer to the Chichibabin reaction. Thus it has been shown that 6-phenylphenanthridine is aminated by sodium amide in liquid ammonia with replacement of the phenyl group by the NH_2 group[226]:



Similarly, 1-methyl-2-phenylbenzimidazole is converted into 2-amino-1-methylbenzimidazole (in 55% yield) on fusion with $NaNH_2$ and into 1-methylbenzimidazolidinone (in 60% yield) on fusion with KOH. This reaction is less characteristic of 2-alkylbenzimidazoles[227,228]. There is little doubt that the phenyl group is eliminated in the form of the carbanion, since benzene is produced in the reaction. It is of interest to note that 2-phenylquinoline and 2-phenylpyridine are aminated at the vacant sites (the 4- and 6-positions respectively). An attempt should be made to discover what result is obtained when these compounds are fused with $NaNH_2$ without a solvent.

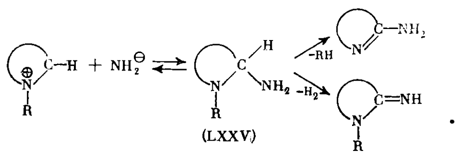
An unusual rearrangement, leading to 2-phenylbenzimidazole, was observed when 2,3-diphenylquinoxaline was acted upon by KNH_2 in liquid ammonia[229]. It has been suggested that the first stage of the process is also the formation of a σ-complex, which then undergoes ring contraction with elimination of one of the phenyl groups as benzylideneamine:



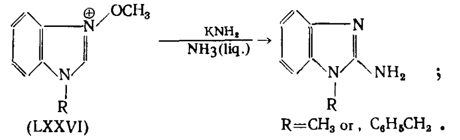
It has been shown recently that the CF$_3$ group in α-trifluoromethyl derivatives of pyridine, quinoline, and isoquinoline is readily substituted by an amino-group on treatment with KNH$_2$ in liquid ammonia[230]. The mechanism of this reaction has been studied[231].

Amination of heteroaromatic cations by metal amides. N-Heteroaromatic cations are known to react with nucleophiles much more readily than neutral molecules, which is frequently used for synthetic purposes. In relation to the Chichibabin reaction, this problem is of fundamental importance in connection with the hypothesis that the pyridine nitrogen atom is coordinated to the Na$^{\oplus}$ ion, as a result of which the heteroatom is partly converted into the onium state. The first data on the interaction of N-heterocyclic cations with metal amides were obtained only recently[232]¶.

If other possible reactions (for example, reactions involving ring opening) are disregarded, adducts of type (LXXV) can be, in principle, stabilised either by the formation of an amine (with elimination of RH) or an imine (with elimination of H$_2$):

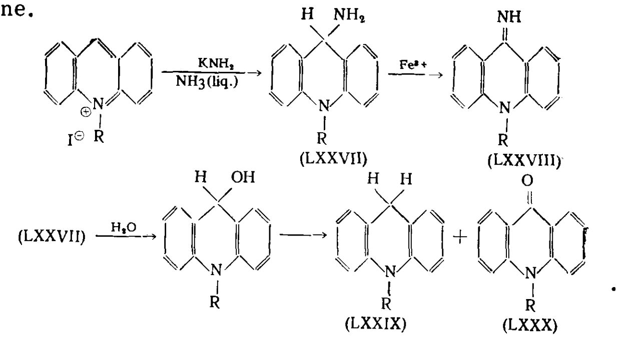


When the first pathway is followed, the N-substituent must be readily eliminated after the addition of the NH$_2^{\ominus}$ anion. It was shown that the N-methoxy-group possesses this ability. Thus, when the salt (LXXVI) is acted upon by KNH$_2$, 1-substituted 2-aminobenzimidazoles are formed in high yields[232]:



The problem of the action of metal amides on the N-oxides of nitrogen-containing heterocycles is very interesting, because the N-oxide group can also activate the addition of a nucleophile and then can be eliminated[184]. Surprisingly, there is so far no information in the literature about the behaviour of N-oxides in relation to metal amides.

The second pathway in the aromatisation of adducts of type (LXXV) constitutes in essence the direct imination reaction. Only one example of such a reaction is known: when the N-methylacridinium cation is acted upon by KNH$_2$ in the presence of Fe(NO$_3$)$_3$, N-methyl-9-acridinone imine (LXXVIII) is formed in 35% yield with approximately the same amount of N-methylacridan (LXXIX) and N-methylacridinone (LXXX).[232] It was not possible to select more effective oxidants in order to increase the yield of the imine.



When metal amides act on 1,3-dialkylbenzimidazolium, naphthimidazolium, 4,5-diphenylimidazolium, and perimidinium salts, mainly the corresponding pseudobases or 2-oxo-derivatives are formed[232]. Thus, despite the possibility, in principle, of the amination and imination of N-heterocycles via their quaternary salts, synthetic methods of general importance have not in essence been developed as yet in this field. The difficulties are to a large extent associated with the selection of solvents, because metal amides are soluble only in liquid ammonia and quaternary ammonium salts are soluble in solvents in which experiments with metal amides are impossible.

Thus there have been significant advances in recent years in the study of all the aspects of the Chichibabin reaction. As regards its mechanism, the formation of σ-complexes has been demonstrated†, the phenomenon of

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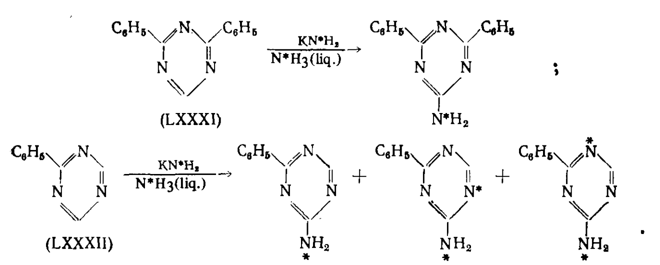
¶ Certain N-heteroaromatic cations[164,233] and bases[167] (pteridine) undergo covalent amination in liquid ammonia even in the absence of amide ions.

† Two papers by Dutch chemists, which report the successful amination in liquid ammonia of diphenyl-1,3,5-triazine (LXXXI) and phenyl-1,3-triazine (LXXXII), have been published recently[234,235]. The reaction is slow (up to 72 h) and requires a large excess of KNH$_2$ (by a factor of 40–50), but the yield of the amine is fairly high (72%):



The formation of hydride σ-complexes as intermediates was noted in both cases. According to the authors, (LXXXI) is aminated exclusively via the addition-elimination mechanism, while the amination of (LXXXII) takes place to an extent of 55% via the *ANRORC* mechanism and to an extent of 45% via the ***AE*** mechanism (demonstrated with the aid of tracer atoms). However, we are dealing in essence, not with a new mechanism of the Chichibabin reaction, but with an unusual behaviour of the σ-complex, capable of ring–chain tautomerism, as a result of which the label enters the ring. On the other hand, the addition and elimination stages themselves probably proceed in the usual way.

bifunctional catalysis in the aromatisation stage has been observed, a study has been made of the influence of substituents on the rate of amination, and the important role of the $>$N → NaNH$_2$ coordination as the initial reaction stage has been elucidated; in connection with the last item, the role of the basicity of the heterocycle, the *ortho*-dimethoxy-effect, the difficulty of γ-amination, etc. have been explained. An important factor is the determination of the relative activities of various types of heteroaromatic systems in the Chichibabin reaction. The applications of the reaction have been extended to perimidine derivatives (the first type of heterocyclic systems with an excess of π electrons which are aminated on treatment with NaNH$_2$) and quinazoline derivatives as well as condensed imidazole systems. It has been possible to introduce into the reaction *N*-heteroaromatic cations, to achieve substitutional amination with elimination of carbanions, and to extend significantly the scope of direct hydroxylation and hydrazination of heterocycles.

At the same time many problems still await solution. Thus the role of radical-anions as intermediates in the amination reaction is still not clear; the problem of the rate-limiting stage of the reaction in an aprotic medium requires elucidation. The search for new types of solvents (apart from liquid ammonia), capable of dissolving even to a slight extent sodium amide, is urgently required; the introduction of crown-ethers as additives appears to be an attractive possibility. One may expect new advances in extending the scope of the Chichibabin reaction to the *N*-oxides of nitrogen-containing heterocycles and new types of heteroaromatic systems.

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Janovsky σ-Complexes

S.S.Gitis and A.Ya.Kaminskii

The methods of preparation, structure, and properties of the coloured products formed in the Janovsky reaction of aromatic polynitro-compounds with acetone and other ketones in an alkaline medium as well as the analogous complexes with other compounds containing mobile hydrogen atoms are examined and the existing ideas about the mechanism of the Janovsky reaction and further transformations of the σ-complexes are discussed.
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I. INTRODUCTION

In 1976 90 years had elapsed since the discovery by the Czech chemist Jaroslav Janovsky of the reaction between *m*-dinitrobenzene and acetone in an alkaline medium. This interaction, which is accompanied by the appearance of a deep colour, has come to be known as the Janovsky colour reaction. It was subsequently extended to various aromatic polynitro-derivatives and ketones. Many investigators have now established that in the majority of cases the colour is due to the formation of σ-complexes—the products of the addition of the nucleophile to the substrate. A number of reviews have been devoted to the structure and properties of anionic σ-complexes[1-6] in which the σ-complexes with acetone and other carbanions are only rarely mentioned. The aim of the present review is to fill the gap in this field. The σ-complexes of aromatic polynitro-compounds with various carbanions can be quite justifiably called "Janovsky σ-complexes". The authors of recently published reviews of the complexes of ketones with polynitro-compounds[7,8] consider mainly the subsequent cyclisation reaction of the Janovsky σ-complexes, which they discovered and investigated (in the present review studies on the structure and properties of the so-called bicyclic complexes are not included).

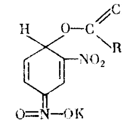
In 1886 Janovsky and Erb[9,10] established that the addition of an alcoholic solution of potassium hydroxide to an acetone solution of *m*-dinitrobenzene (*m*-DNB) causes the appearance of a violet colour. Subsequently, Janovsky[11], Wilgerodt[12], and many other investigators extended this sensitive colour reaction to many ketones and aldehydes[13-19] and also various polynitro-compounds[13,17,20-25]. A series of empirical rules were derived[14,23-25] and it was shown that not only *meta*- but also *ortho*- and *para*-dinitrobenzenes[26] as well as many mononitro-compounds containing an electron-accepting substituent in the *meta*-position with respect to the nitro-group[27,28] tend to undergo the Janovsky reaction.

Apart from alkalis, weak bases such as sodium carbonate or iodide may be used to establish an alkaline medium[29].

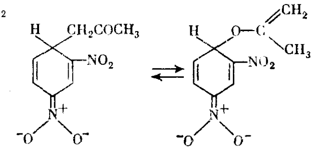
II. INTERACTION OF AROMATIC NITRO-COMPOUNDS WITH ACETONE IN THE PRESENCE OF ALKALI

1. σ-Complexes of *m*-Dinitrobenzene and Its Derivatives

The study of the absorption spectra[23,25,30-36] of solutions of the coloured products of the Janovsky reaction enabled a number of workers[23,25,30] to put forward a hypothesis concerning their structure. Baernstein[30] suggested that the reaction involves the addition of the enolic form of the ketone to the *aci*-form of the nitro-compound with formation of product (I). Canbäck[23,25] believed that real covalent C–C or C–O bonds are not formed in coloured products of types (II) and (III) and that the linkage between *m*-DNB and the acetone residue is one between a dipole and an anion. Subsequently evidence was adduced in support of both the enolic form (III)[21,22,26,36] and the keto-form (II)[14,37,38].



(I)



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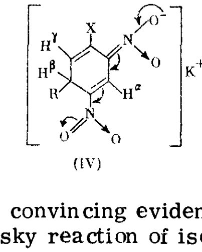

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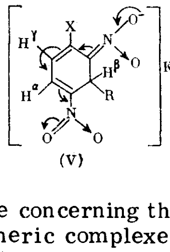


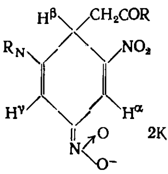
(V)

The first convincing evidence concerning the formation in the Janovsky reaction of isomeric complexes (IV) and (V), differing in the site of addition of the acetone residue, was presented by Gitis and coworkers[39-41]. Having observed the absence of a colour in the case of 2,4-dinitromesitylene, they investigated a large number of model compounds in which the substituent X prevents the addition of the acetone residue R to the carbon atom linked to the substituent. When the 3- and 5-positions in the molecule of a 1-X-2,4-dinitro-compound are vacant, both complexes, (IV) and (V), are formed in all cases and the absorption spectra show two maxima. If the 3-position is occupied by a substituent, complex (IV) is formed and the spectrum shows only the short-wavelength absorption maximum (λ_{max} = 550–570 nm). The introduction of a substituent into the 5-position leads to the formation of complex (V) only, which gives rise to the long-wavelength absorption maximum (λ_{max} = 600–690 nm). This product is less stable and cannot be detected for certain *m*-DNB derivatives containing an electron-donating substituent X.

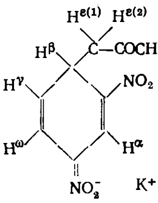
The conclusions reached about the structure of the coloured Janovsky complexes[39,40] were confirmed by studies of the influence of substituents on the positions of both absorption maxima (Table 1) using correlation analysis[41-43]. Analogous conclusions concerning the correspondence of the absorption maxima to definite coloured reaction products were arrived at somewhat later by Pollitt and Saunders[43,44], who believe[43] that the hypsochromic shift of the two absorption maxima, caused by the majority of substituents, is due to the displacement of the nitro-groups from the plane of the ring. According to their view[44], direct attack by the HO^- ion on the polynitro-compound is possible together with the formation of Janovsky complexes in dimethylformamide and the assignment of the bands in the absorption spectra is difficult, particularly for electronegative substituents.

Thus, using model compounds, various investigators came close to the determination of the structure of the products of the above reaction with the aid of electronic absorption spectra. The final answers to a number of questions concerning the detailed structure of the coloured complexes were obtained as a result of their isolation in a free form and their investigation by ^{1}H NMR and infrared spectroscopy.

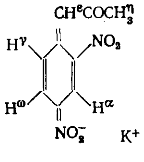
The first attempts[14,15,36,38] to isolate these products were unsuccessful—in all cases the decomposition products of the Janovsky complexes and not the complexes themselves were obtained. The first successful synthesis of this kind was achieved by Akatsuka, who was able to obtain the dark-violet products of the addition of acetone and acetophenone to 3,5-dinitrobenzenesulphonic acid[45] and 3,5-dinitrobenzoic acid[46] in the presence of K_2CO_3. The reaction products were identified by elemental analysis, paper chromatography, and their conversion into *S*-benzylthiuronium salts[47], which made it possible to attribute to them structure (VI):



(VI)



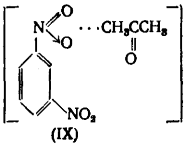
(VII)



(VIII)

$R_N = SO_3^-$ or COO^-

R=CH_3 (a) or C_6H_5(b)



(IX)

Table 1. The electronic spectra of Janovsky σ-complexes obtained from *m*-DNB derivatives in acetone.

X	λ_1, nm	lg ε_1	λ_2, nm	lg ε_2	λ_1, nm	lg ε_1	λ_2, nm	lg ε_2	Refs.
Isomeric σ-complexes of 1-X-2,4-dinitrobenzenes									
	(IV)				(V)				
H	572	4.28	—	—	689, 692	—	—	—	51, 39, 44
H^a	555	4.03	—	—	—	—	—	—	56
H^b	587	4.29	—	—	—	—	—	—	51, 56
H^c	582	3.75	—	—	—	—	—	—	51, 56
CH_3	573	4.28	335	4,079	670, 662	—	—	—	60, 39, 65
CH_3	563, 580	4.15	—	—	665	—	—	—	65, 68, 44
C_2H_5	568, 565	4.19	—	—	670	—	—	—	23, 63
$CH(CH_3)_2$	567	4.26	—	—	678	—	—	—	63, 65
$C(CH_3)_3$	564	4.08	—	—	680	—	—	—	63, 65
CH_2COO^-	576	3.88	—	—	—	—	—	—	23
CH_2COOCH_3	579	4.05	—	—	—	—	—	—	23
OCH_3	562, 550	4.35	354	4,079	625, 626	4.32	338	4.54	60, 65, 40
OC_2H_5	561	—	—	—	626	—	—	—	40
OC_6H_5	571, 561	—	—	—	638	—	—	—	40, 23
OCF_3	545	—	—	—	647	—	—	—	40
F	570, 562	—	—	—	641, 633	—	—	—	44, 40
Cl	545, 561	4.34	376	—	668, 665	—	360	—	23, 82
Cl	548	—	—	—	666, 660	—	—	—	44, 40
Br	545, 560	—	—	—	663, 675	—	—	—	40, 23, 44
I	550	—	—	—	672	—	—	—	40
CN	548	—	—	—	705	—	—	—	44
CN^c	551	—	370	—	—	—	—	—	44
$COOCH_3^c$	552	—	358	—	—	—	—	—	44
$COOCH_3$	560, 567	4.42	376	4,009	686, 685	4.25	357	4.62	60, 23, 44
$COOCH_3^d$	558	4.45	372	4,065	686	4.26	354	4.61	60
SC_2H_5	578	4.52	396	4,350	568	4.48	362	4.45	60
SCN	560	4.36	380	4,190	660	4.21	342	4.27	60
NH_2^e	522, 525	4.12	385	—	—	—	—	—	40, 65
NH_2^e	529	—	398	—	—	—	—	—	44
$NHNH_2$	568, 570	3,62	—	—	—	—	—	—	23, 40
$NHCOCH_3^e$	425	4.35	—	—	—	—	—	—	23
Isomeric σ-complexes of 1-X-3,5-dinitrobenzenes									
	(XI)				(X)				
CH_3	584, 580	4.52	360	4,24	—	—	—	—	60, 44
CH_3^c	588	—	360 & 372^f	—	—	—	—	—	44
OCH_3	590	4.35	360	4,24	—	—	—	—	44, 60
OCH_3^c	603	—	360 & 372^f	—	—	—	—	—	44
Cl	563	—	—	—	—	—	—	—	44
Cl^c	570	—	365	—	726	—	379	—	44
CN	549, 530	4.10	396	—	631	—	—	—	44, 58
CF_3	533	4,40	373	—	639	4.26	373	—	60
COO^-	568, 563	—	380	—	660	—	—	—	44, 23
COO^{-c}	580	—	406	—	640	—	—	—	44
$COOCH^g$	547	4,15	417	4,15	560	—	410	—	62
$COOCH_3$	561	—	—	—	625	—	406	—	44
$COOCH_3^b$	545, 572	—	414	—	630	—	407	—	59, 44
$COOC_2H_5$	558	4.48	424	4,39	628	4 41	408	4.62	60
	563	—	—	—	625	—	406	—	44
$CONH_2$	580	—	—	—	640	—	403	—	44
$CONH_2$	580	—	404	—	650	—	—	—	44
$CON(CH_3)_2$	553	4,23	385	4,04	—	—	—	—	62
Isomeric σ-complexes of 1-X-3,5-dinitrobenzenes									
	(XI)				(X)				
$CON(C_2H_5)_2$	582	—	399	—	656	—	—	—	44
CON⟨H⟩	560	4.11	385	3.78	655	4.00	407	3.90	62
SO_2OCH_3	555	2.88	—	—	—	—	—	—	45—47
$SO_2OC_6H_5$	555	3.92	—	—	—	—	—	—	45—47
NH_2	—	—	—	—	624	—	—	—	44
$N(CH_3)_2$	—	—	—	—	614	—	—	—	44
$N(CH_3)_2^c$	—	—	—	—	625	—	377	—	44

a) Ethanol (lg ε = 4.076 in tetrahydrofuran); *b*) DMSO; *c*) DMF; *d*) $(n\text{-}C_4H_9)_4\overset{+}{N}$ cation; *e*) it has been shown[40,44] that the formation of a colour in the presence of these substituents is due to the elimination of a hydrogen atom from the amino-group and the formation of the 2,4-dinitrophenylanilinium ion; *f*) double maximum; *g*) acetone + 10% of methanol.

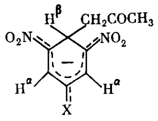
Gitis and Kaminskii[48] developed a spectrophotometrically monitored synthesis of classical Janovsky complexes from *m*-DNB, 1,3,5-trinitrobenzene (TNB), and then 2,4-dinitroanisole[49]. It was established[48,50] that they are σ-complexes of type (VII), where the acetone residue adds in the keto-form to a ring carbon atom with formation of a covalent C–C bond. This is confirmed by the presence in the infrared spectra of the ν(C=O) band at 1710 cm^{-1}, whose position and intensity are close to those of the ν(C=O) band of 2,4-dinitrophenylacetone. Furthermore, a small amount of 2,4-dinitrophenylacetone was detected together with the initial *m*-DNB in the products of the acid decomposition of complex (VII).[50] By treating an acetone solution of *m*-DNB with solid KOH, Kimura et al.[51] also isolated the Janovsky complex (VII), whose structure was demonstrated by elemental analysis and by comparison with the specially prepared potassium salt of 2,4-dinitrophenylacetone (VIII).

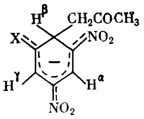
Contrary to generally accepted ideas, Ryzhova and coworkers[52–54] suggest that the products of the interaction of *m*-, *o*-, and *p*-dinitrobenzenes, which they obtained in the presence of KOH by reaction with acetone, acetophenone, cyclohexane (cyclohexanone?), and ethyl methyl ketone and which have the 1 : 1 and 1 : 2 compositions, are donor–acceptor complexes of type (IX), formed as a result of the local interaction of the ketone with the nitro-group. However, the evidence presented by these workers[54] in support of structure (IX) cannot be regarded as convincing; it conflicts with all the available data concerning the structure of Janovsky complexes.

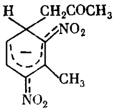
The ^{1}H NMR spectrum of a Janovsky σ-complex of *m*-DNB was studied for the first time by Fyfe and Foster[55], who obtained this complex by adding solid sodium methoxide to a solution of *m*-DNB in a 1 : 1 mixture of acetone and dimethyl sulphoxide (DMSO). The structure of the σ-complex (VII) was confirmed by its characteristic chemical shifts and spin–spin coupling constants: $\delta = 8.32$ (H^α), 4.17 (H^β), 5.38 (H^γ), and 6.6 p.p.m. (H^ω); $J_{\alpha,\omega} = 1.9$ and $J_{\gamma,\omega} = 10.2$ Hz. The $H^{\epsilon(1)}$ and $H^{\epsilon(2)}$ methylene protons are non-equivalent owing to the lack of symmetry of the $C_{(1)}$ atom. As a result of the spin–spin coupling with H^γ, $H^{\epsilon(1)}$ and $H^{\epsilon(2)}$, the signal due to the H^β nucleus is therefore a quintet; $J_{\beta,\gamma} = J_{\beta,\epsilon(1)} = 5.0$ and $J_{\beta,\epsilon(2)} = 10.0$ Hz. This assignment of the signals is confirmed by the ^{1}H NMR spectrum of the analogous complex obtained from hexadeuteroacetone. In the reaction solutions investigated no isomers of type (V, X = H) were detected. The σ-complex (VII) was isolated in a free form[56] by treating an acetone solution of *m*-DNB with potassium hydroxide and subsequent precipitation with benzene. The infrared spectrum of the complex showed absorption bands at 1719 cm^{-1} (C=O), 1290 cm^{-1} (*sym*.NO_2^-), and 1610 cm^{-1} (C=C).

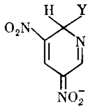
The electrochemical reduction of the σ-complex (VII) at the potential of the first reversible reduction wave (~ 1.0 V) in acetone in the presence of $(n\text{-}Bu)_4NClO_4$ as the supporting electrolyte made it possible to obtain for the first time[57] its radical-dianion, which was detected by ESR. The large difference between the splittings due to the ^{14}N nuclei confirms the non-equivalence of the nitro-groups and the quinonoid structure of the complex.

The structure and properties of the σ-complexes of acetone with various *m*-DNB derivatives have been studied in detail by ^{1}H NMR and infrared spectroscopy. Initially these complexes were investigated in reaction solutions and then most of them were isolated in a free form. Thus Foreman and Foster[58] showed that, when acetone solutions of 1-X-3,5-dinitrobenzenes (X = COOMe and COO$^-$) are treated with triethylamine or sodium methoxide, the σ-complex (X) is formed initially, but after several days is converted into a 7 : 1 equilibrium mixture of isomers (X) and (XI):


(X)


(XI)


(XII)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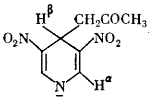
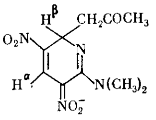

(XIV)


(XV)

Y = OCH_3 (a) or
CH_2COCH_3 (b) ,

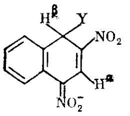
This is consistent with the results obtained for X = CF_3 and CN.[59] The exchange interaction of σ-complexes containing other substituents with the free radicals formed in the reaction mixture leads to a broadening of the signal and, when diethylamine is used[59], the exchange altogether precludes the measurement of the ^{1}H NMR spectrum.

Such broadening does not occur in the study of the ^{1}H NMR spectra of complexes isolated in a free form. Because of this, Gitis and coworkers were able to investigate a large number of σ-complexes of *m*-DNB derivatives, obtained by the spectrophotometrically monitored synthesis which they developed previously[48]. Analysis of the electronic, ^{1}H NMR, and infrared spectra of the σ-complexes of a series of 1-X-3,5-dinitrobenzenes (X = Me, OMe, COOEt, or CF_3 [60,61] and X = COOMe, $CONC_5H_{10}$, $CONMe_2$, or $CONH_2$ [62]) also confirmed (Table 2) that they are a mixture of isomers (X) and (XI), with the latter predominating; the stability of the complexes increases with enhancement of the electron-accepting properties of the substituent. The σ-complexes of a series of 1-alkyl-2,4-dinitrobenzenes[63–65] (alkyl = Me, Et, iso-Pr, or t-Bu) and a series of 1-X-2,4-dinitrobenzenes[60,65] (X = OMe, COOMe, SEt, or SCN) were obtained by a similar procedure. In the latter case the formation of two isomeric complexes of types (IV) and (V), differing in the site of addition of the acetone residue (R = CH_2COCH_3), established previously on the basis of electronic absorption spectra[39,40], was finally demonstrated with the aid of ^{1}H NMR and infrared spectra. Complex (IV) is more stable owing to the presence in the *para*-position with respect to the rehybridised carbon atom of a powerful electron acceptor (the nitro-group). The type (V) isomer with X = OMe is extremely unstable and, when X = H or alkyl, it cannot be obtained in a free form at all. Enhancement of the electron-accepting properties of the substituent increases the stability of this complex; for X = COOMe, it was isolated[60] in a mixture with isomer (IV). It is noteworthy that, for sulphur-containing substituents (X = SCN or SEt), the opposite behaviour is observed: isomer (V) becomes more stable than isomer (IV).

It has recently been possible to isolate in a free form[66] extremely labile σ-complexes of 1-halogeno-2,4-dinitrobenzenes (halogen = F, Cl, Br, or I), which, according to ^{1}H NMR, infrared, and electronic spectroscopic data, are also mixtures of isomers of types (V) and (IV) with the latter predominating (with the exception of the fluorine-containing complex). The synthesis of a series of σ-complexes from *m*-DNB derivatives showed that the spectra contain new maxima in the near ultraviolet in addition to the absorption maxima in the visible region known previously[40–42] (Table 1). On the basis of the successful[67] chromatographic separation of isomers (X) and (XI) with X = COOEt and the resolution of the overlapping bands into their components, the short-wavelength maximum in the ultraviolet region was assigned to isomers of type (V) (λ_{max} between 338 and 350 nm for different substituents X) and type (X) (λ_{max} = 360–408 nm), while the long-wavelength maximum was assigned to isomers of type (IV) (λ_{max} = 354–396 nm) and type (XI) (λ_{max} = 360–424 nm) (Table 1). The resolution of the bands using the characteristics of the complexes isolated made it possible to observe[68] in the spectra of the reaction solutions an absorption maximum for 2,4-dinitroanisole (λ_{max} = 625 nm) corresponding to the unstable isomer (V, X = OMe) and a maximum at 515 nm for 2,6-dinitrotoluene corresponding to a product of the transformation of the σ-complex (XII).

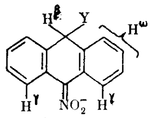
A number of studies[58–68] showed that the presence of electron-accepting groups in the molecule of the *m*-DNB derivative increases the stability and hence the yield of the σ-complexes formed. Both isomers of the σ-complexes derived from 1-X-3,5-dinitrobenzenes, (X) and (XI), are much more stable than the corresponding isomers (V) and (IV) obtained from 1-X-2,4-dinitrobenzenes. The σ-complexes of 3,5-dinitropyridine with acetone[69], formed as a mixture of isomers (XIIIb) and (XIV) with the latter predominating (λ_{max} = 519 nm) following the addition of acetone to a solution of the alkoxide complex (XIIIa) in DMSO, are still more stable. On the other hand, solvolysis by acetone of the methoxide complex of 2-dimethylamino-3,5-dinitropyridine results in the formation[69] of a single acetone σ-complex, probably having structure (XV), with characteristic signals at δ = 8.14 and 5.1 p.p.m. for H^{α} and H^{β} respectively[69].

Stabilisation of the same type owing to the electron-accepting properties of condensed aromatic rings enabled Foster and coworkers[70] to obtain fairly readily the σ-complexes of 1,3-dinitronaphthalene (XVIa) and 9-nitroanthracene (XVIIa) by treating their acetone solutions with triethylamine. The structures of these σ-complexes were demonstrated on the basis of the ^{1}H NMR spectra of their solutions [(XVIa): δH^{α} = 8.76 p.p.m., δH^{β} = 4.81 p.p.m., $J_{\alpha,\beta} \simeq$ 1 Hz; (XVIIa): δH^{β} = 4.29 p.p.m., δH^{γ} = 8.72 p.p.m., δH^{ω} = 7.16 p.p.m.].



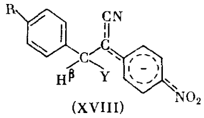
(XVI)

Y = CH$_2$COCH$_3$ (a) or CH$_2$NO$_2$ (b);



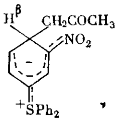
(XVII)

Y = CH$_2$COCH$_3$ (a) or CH(CN)$_2$ (b);



(XVIII)

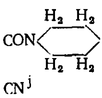
Y = CH$_2$COCH$_3$ (a) or OCH$_3$ (b)



(XIX)

When acetone solutions of 4′-substituted α-cyano-4-nitrostilbenes (R = NO$_2$ or Me) were treated with sodium methoxide, the corresponding σ-complexes (XVIII) were obtained[71]. The observed absorption maxima (λ_1 = 543 nm, λ_2 = 576 nm) correspond to products of the addition of the acetone residue to the double bond (XVIIIa), which in the authors view are formed from the alkoxide addition products (XVIIIb). The ^{1}H NMR spectra of the reaction solutions indicate the presence of a single adduct of type (XVIII) regardless of the *cis*- or *trans*-structure of the initial 4-nitrostilbene.

Table 2. ^{1}H NMR spectra of the Janovsky σ-complexes obtained from *m*-DNB and its derivatives (R = CH$_2$COCH$_3$) in [D$_6$] dimethyl sulphoxide.

X	Isomer	δH^{α} (doublet)	δH^{β} (triplet)	δH^{γ} (doublet)	$J_{\alpha,\beta}$	$J_{\alpha,\gamma}$	$J_{\beta,\gamma}$	Refs.
				From 1-X-2,4-dinitrobenzenes[a]				
H[b]	(VII)[b]	8.32	4.17	5.38	0.6	—	5.0	55
H	(VII)[d]	8.26	4.17	5,36	—	—	4.5	56, 131
CH$_3$	(IV)	8.40	3.93	5,45	—	—	6,6	63, 65
C$_2$H$_5$	(IV)	8.41	4.04	5.12	—	—	6.0	63
CH(CH$_3$)$_2$	(IV)	8.45	4.05	5.20	—	—	6.0	63, 65
C(CH$_3$)$_3$	(V)	8.39	4.05	5.07	—	—	5,6	63, 65
OCH$_3$	(IV)	8.33	4.09	4.46	0.8—1.5	—	5.8	60, 65
	(V)	7.42	5.07	5.07	0.8—1.5	8.5	—	60, 65
F	(IV)	8.31	4.18	4.89	—	—	5.7	66
	(V)	7.47	5.17	4.95	—	8.5	—	66
Cl	(IV)	8.45	4.09	5.75	—	—	6.5	66
	(V)	7.08	5.50	5.43	—	8.0	—	66
Br	(IV)	8.42	4.09	5.75	—	—	6.5	66
	(V)	7.08	5.50	5.43	—	8.0	—	66
I	(IV)	8.38	3.98	6.12	—	—	—	66
	(V)	7.00	5.91	5.65	—	7.7	—	66
COOCH$_3^e$	(IV)	8.21	4.14	5.50	0.8—1.5	—	5.5	60, 65
	(V)	7.43	5.08	5.06	0.8—1.5	7.6	—	60, 65
SC$_2$H$_5$	(IV)	8.36	4.16(m)	4.91	0.8—1.5	—	5,8	60, 65
	(V)	7.32	5.14	5.25	0.8—1.5	8.3	—	60, 65
SCN	(IV)	8.21	4.25	5.64	0.8—1.5	—	5.8	60, 65
	(V)	7.49	5.08	5.60	0.8—1.5	7.8	—	60, 65
OCH$_3^f$	(IV)	8.43	4.13	4.52	—	—	—	137
	(V)	7.56	5.01	5.10	—	—	—	137
				From 1-X-3,5-dinitrobenzenes[g]				
CH$_3$	(XI)[h]	8.35	4.14	6.47	0.8	2.0	2.0	60, 61
OCH$_3$	(XI)[h]	8.20	4.21	5.83	1.5	1.6	—	60, 61
CN	(XI)[d]	8.05	4.24	7.17	0.8	2.0	—	58
	(X)[d]	7.40	4.91	—	0.8	2.0	—	58
CF$_3$	(XI)[h]	8.37	4.54	7.32	1.0	2.0	2.0	60, 61
	(XI)[d]	7.95	4.29	7.00	—	2.0	—	58
	(X)[h]	7.64	5.18	—	0.5	—	0.5	61, 67
	(X)[d]	7.32	4.91	—	—	—	—	58
COOH	(XI)[d]	8.35	4.68	7.58	1.0	2.0	—	59
	(X)[d]	8.23	5.10	—	1.0	—	—	59
COOCH$_3$	(XI)	8.27	4.61	7.80	1.0	1.9	—	62
	(XI)[d]	8.31	4.61	7.82	1.0	2.0	—	59
	(X)	8.02	5.06	—	0.8	—	—	62
	(X)[d]	7.87	6.22	—	1.2	—	—	59
COOC$_2$H$_5$	(XI)[h,i]	8.36	4.65	7.87	1.1	2.0		60, 61
	(X)[h,i]	8.09	5.09	—	0.8	—	0.8	60, 61
CON(CH$_3$)$_2$	(XI)	8.29	4.63	6.80	1.0	1.7	—	62
	(X)	7.75	5.09	—	0.7	—	—	62
	(XI)	8.25	4.56	6.73	0.8	1.8	—	62
	(X)	7.69	5.07	—	1.0	—		62
CN[j]	(XI)	8.18	4.33	7.35	—	2.0	—	59
	(X)	7.55	4.50	—	—	—	—	59
CN[k, l]	(XI)	8.29	4.82	7.42	—	1.9	0	111
	(X)	7.55	5.40	7.64	—	—	—	111
COOCH$_3^{k, m}$	(XI)	8.29	4.82	7.72	1.2	1.8	—	111
	(X)	7.96	5.29	8.04	1.0	1.0	—	111
CONC$_5$H$_{10}^{k, n}$	(XI)	8.26	4.78	6.66	1.0	2.0	—	111

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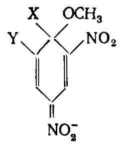
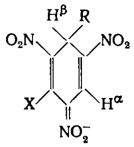
a) usually δ(CH$_2$) = 3.10–3.20 p.p.m., δ(CH$_3$) = 2.05–2.15 p.p.m., and $J_{\beta CH_2} \simeq$ 5.0 Hz for the added acetone residue; *b*) δH^{ω} = 6.57 p.p.m., $J_{\alpha,\omega}$ = 1.9 Hz, $J_{\gamma,\omega}$ = 10.2 Hz, and $J_{\beta,\omega}$ = 1.0 Hz; *c*) in a 1 : 1 acetone–DMSO mixture; *d*) in DMSO; *e*) all the signals are the same for the (n-C$_4$H$_9$)$\overset{+}{N}$ K$^+$ cations; *f*) complexes with acetonitrile (R = CH$_2$CN), λ_{max}(CH$_3$CN) = 590 nm (IV) and 618 nm (V); *g*) δ(CH$_2$) = 2.37–2.50 p.p.m., δ(CH$_3$) = 2.02–2.14 p.p.m., J_{β,CH_2} = 6.0–4.0 Hz (XI), and J_{β,CH_2} = 5.6–5.0 Hz (X) for the added acetone residue; *h*) in [D$_6$] acetone; *i*) signals due to the C$_2$H$_5$ group in isomers [δ(CH$_2$) = 4.13 p.p.m. and δ(CH$_3$) = 1.21 p.p.m. for (XI); δ(CH$_2$) = 4.11 p.p.m. and δ(CH$_3$) = 1.19 p.p.m. for (X)]; *j*) complex with C$_2$H$_5$COC$_2$H$_5$, $J_{\beta,CH_2} \simeq$ 4.0 Hz; *k*) complexes with cyclohexanone; *l*) J_{β,CH_2} = 1.5 Hz (XI) and 7.0 Hz (X), λ_{max} = 640 nm (X) and 540 nm (XI); *m*) J_{β,CH_2} = 6.5–6.0 Hz, λ_{max} = 625 nm (X); *n*) J_{β,CH_2} = 2.0 Hz, λ_{max} = 550 nm.

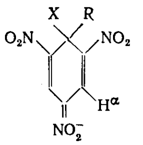
The formation of Janovsky σ-complexes from mononitrobenzenes was demonstrated by Reutov and coworkers[72] who obtained a solution of the σ-complex (XIX) (λ_{max} = 490 nm; lg $\epsilon \simeq 4.25$) by adding an alcoholic solution of KOH to an acetone solution of *m*-nitrophenyldiphenylsulphonium fluoroborate. Its structure was demonstrated with the aid of ^{1}H NMR spectra (δH^β = 5.80 p.p.m., δH_{Ar} = 8.0–7.4 p.p.m.) and also by synthesising the same product by the reaction of the initial substrate with $CH_3COCH_2.HgCl$ in the presence of Bu_4NI.

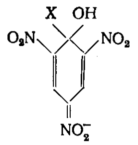
2. Janovsky σ-Complexes of 1,3,5-Trinitrobenzene and Its Derivatives

In studies of the structure of the coloured products of the interaction of *sym*-TNB and its derivatives with acetone in an alkaline medium many workers compared their absorption spectra with those of Meisenheimer σ-complexes, for which a structure of type (XX, Y = NO_2, X = OMe) was regarded as generally accepted[1-6]:


(XX)

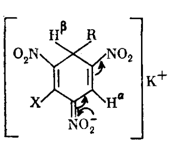

(XXI)

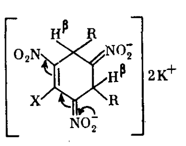

(XXII)

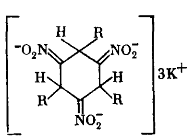

(XXIII)

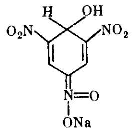
Thus Kimura[73] suggested that the bands observed for 1-X-2,4,6-trinitrobenzenes in an acetone–methanol mixture in the presence of alkali (λ_1 = 450 nm and λ_2 = 520–530 nm) are due to the products (XXI)–(XXIII) (R is the acetone residue). When X = H, Cl, Me, OMe, OEt, or NEt_2, structure (XXI) is characteristic of the complexes and, when X = OPh, COOH, or COOEt, the latter has structure (XXII). Having established the similarity of the absorption spectra of picryl chloride[74,75] and tetryl in water, methanol, and acetone in the presence of alkali, Abe concluded[75-77] that in both cases the colour is due to product [XXIII, X = Cl or $N(NO_2)Me$]. Pollitt and Saunders[44] suggested that, of the three bands (462, 570, and 518 nm) observed for *sym*-TNB, the first two correspond to a 1 : 1 complex and the third is due to side products. Spectroscopic determination of the composition of the complex of 2,4,6-trinitrobenzoic acid (TH) with acetone (HA) (1 : 2) enabled Neufer et al.[78] to ascribe to it the structure $TH.A^- + H_2A^+$.

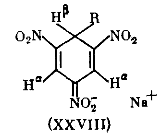
Detailed spectrophotometric studies[39,79] showed that, of the three structures (XXIV), (XXV), and (XXVI) proposed[39] for the products derived from *sym*-TNB, only one is actually formed, namely (XXIV, X = H). It is fairly stable and has two maxima in the visible region (at 462 and 568 nm) with an intensity ratio of 2 : 1. On the other hand, in the presence of a large excess of alkali[80] additional maxima appear at 430 and 518 nm, corresponding to the formation of the product of the addition of a hydroxide ion to a molecule of the trinitro-derivative (XXIII, X = H). When potassium methoxide is used as the alkaline agent, the complex (XX, X = H, Y = NO_2) is formed together with (XXI, X = H).


(XXIV)


(XXV)


(XXVI)


(XXVII)


(XXVIII)

R = $CH_2^\epsilon COCH_3^\eta$ (a) or $CH_2COC_6H_5$ (b)

Owing to the greater stability of the σ-complexes obtained from *sym*-TNB compared with the complexes of *m*-DNB, studies on their synthesis have been more successful. Thus, by allowing an acetone solution of *sym*-TNB to react with NaOH, Giua[81] isolated a red-brown crystalline product. The author believed that in this case an NaOH molecule adds on and the compound has the structure (XXVII). However, the data available at present suggest that in reality he isolated for the first time the Janovsky σ-complex of *sym*-TNB (XXVIIIa). By allowing solid sodium bicarbonate to react with an acetone solution of *sym*-TNB, Kimura[82] obtained a σ-complex, to which he attributed the structure (XXVIIIa) on the basis of analysis and determination of the molecular weight. He obtained the analogous acetophenone complex (XXVIIIb) from an alcoholic solution[51]. By carrying out the reaction in an indifferent solvent, Gitis[26] obtained products of the addition of two and three molecules of the sodium derivative of acetone to di- and tri-nitro-compounds in the form of amorphous brown powders, which are rapidly converted into a tar in air. By treating acetone solutions of *sym*-TNB and some of its derivatives with concentrated aqueous ammonia and subsequently evaporating the solvent *in vacuo*, Abe[75] isolated dark-red crystalline substances and suggested that they are products of the addition of ammonium hydroxide to polynitro-compounds (XXIII). A stable σ-complex of *sym*-TNB with acetone was isolated as a result of a spectrophotometrically monitored synthesis[48]; it was shown[48,50] that it has the structure (XXVIIIa), in which the acetone residue in the keto-form is attached to a ring carbon atom.

Foster and Fyfe[83] established that, when the methoxide complex of *sym*-TNB (XX, X = H, Y = NO_2) is dissolved in acetone, the methoxy-group is replaced by the conjugate base of the solvent with formation of the corresponding Janovsky complex (XXVIIIa). The signal of the H^β proton in its ^{1}H NMR spectrum at 5.18 p.p.m. is split into a triplet (J = 9 Hz) owing to the interaction with neighbouring methylene protons; the signal due to the ring protons H^α at 8.47 p.p.m. consists of a doublet (J = 1 Hz). A similar substitution occurs when an acetone solution of *sym*-TNB is acted upon by sodium methoxide. If the substitution is carried out in hexadeuteroacetone, a broad unresolved band at 5.18 p.p.m. is observed for H^β, which indicates the formation of the σ-complex (XXVIII, R = CD_2COCD_3). When trimethyl- or triethyl-amine was added to an acetone solution of *sym*-TNB, the σ-complex (XXVIIIa) was isolated in a free state[84]. This made it possible to assign the signals of the attached acetone residue (δH^ϵ = 2.65 p.p.m., J = 5 Hz; δH^η = 2.15 p.p.m.) and the cation $H\overset{+}{N}Me_3$ (δ = 2.85 p.p.m.) in the ^{1}H NMR spectra. The positions of the signals in the ^{1}H NMR spectrum and of the absorption maxima in the electronic spectra (λ_1 = 557–572 nm and λ_2 = 460–465 nm) as well as their intensities change somewhat as a function of the nature of the cation (Table 3). Similarly the interaction of *sym*-TNB with diethylamine and other secondary amines[85] leads to the formation of σ-complexes of type (**XXVIII**) with the $H_2\overset{+}{N}R_2$ cation. However, the authors showed that in this case the reaction is accompanied by the formation of a whole series of side and intermediate products.

In the reaction of the organomercury derivatives of acetone $(CH_3COCH_2)_2Hg$ and $CH_3COCH_2.HgX$ with *sym*-TNB in the presence of NaI in DMSO Beletskaya et al.[86] detected by ^{1}H NMR the formation of the σ-complex (**XXVIIIa**) in a high yield via the mechanism

$$CH_3COCH_2HgX + sym\text{-}TNB + 2NaI \rightarrow (XXVIIIa) + HgIX \cdot NaI \ . \qquad (1)$$

The resulting complex is stable in solution for a long time and its ^{1}H NMR spectra agree with those described in the literature[83,84]. The σ-complex (**XXVIIIa**) was obtained by a similar procedure as a result of the interaction of the organotin derivative of acetone $CH_3COCH_2.Sn(CH_3)_3$ with *sym*-TNB in DMSO, as shown by the ^{1}H NMR spectrum[88].

In the study of the structure of Janovsky σ-complexes obtained from *sym*-TNB derivatives one of the fundamental controversial problems is the site of addition of the acetone residue: to an unsubstituted ring carbon atom in polynitrobenzene or to a carbon atom attached to a substituent. Thus, as a result of the study of the interaction of substituted 1-X-2,4,6-trinitrobenzenes (X = OEt, OPh, Cl, or NMe_2) with acetone in the presence of amines, Foster et al.[70] showed that, in contrast to Kimura's ideas[73], the acetone residue adds to an unsubstituted ring carbon atom with formation of compound (**XXI**). According to their data, an acetone solution of picryl chloride and triethylamine gives rise to an ^{1}H NMR spectrum corresponding to structure (**XXI**, X = Cl) and not (**XXII**, X = Cl) (triplet with δ = 5.2 p.p.m. and J = 6 Hz).

Kimura et al.[89] isolated by thin-layer chromatography the products formed when acetone solutions of 2,4,6-trinitroanisole and phenyl 2,4,6-trinitrophenyl ether are acted upon by sodium methoxide. The structure of the σ-complex (**XXI**, X = OCH_3) was demonstrated by ^{1}H NMR (Table 3) and by the fact that its decomposition in an acid medium yielded 3-acetonyl-2,4,6-trinitroanisole. The same workers[90] investigated analogous σ-complexes of picryl chloride and sodium 2,4,6-trinitrobenzenesulphonate. They believe that the Janovsky reaction results in both cases in the formation of the σ-complexes (**XXI**, X = Cl or $NaSO_3$) and, when X = $NaSO_3$, also a small amount of (**XXII**).

The problem of the site of addition of the acetone residue to 1-X-2,4,6-trinitrobenzenes was finally solved in a series of studies[91,92]. It was shown[90] that, when the σ-complex of *sym*-TNB with KOH (XXIII, X = H) is acted upon by acetone, the HO^- ion is displaced by the acetone residue. This is indicated by the change in the electronic spectra [the maxima at 440 and 520 nm are converted into the maxima at 470 and 574 nm corresponding to the σ-complex (**XXI**)] and by the identification of complex (**XXI**) by ^{1}H NMR and infrared spectra. The products of the addition of acetone to 1-X-2,4,6-trinitrobenzenes (X = Me, OMe, COOH, COOMe, COO^-, Cl, or SMe) were isolated in a free state[92] and their structure, like that of the σ-complexes (**XXI**), was confirmed by elemental analysis, ^{1}H NMR, and infrared spectra (Table 3). Thus the acetone residue always adds to an unsubstituted carbon atom regardless of the electron-donating or electron-accepting nature of the substituent. According to the authors[92], the steric hindrance to the incorporation in the ring of the fairly bulky CH_2COCH_3 substituent plays the main role here. The C–CH_2 bond formed in this process is stronger than the C–O bond in the Meisenheimer complexes (**XX**), which prevents the isomerisation of the Janovsky σ-complexes (**XXI**) to complexes (**XXII**). Both these factors are more significant than the stabilisation of the σ-complex (**XX**) or (**XXII**) caused by the energy gain as a result of the weakening of the steric interactions of the substituent X with neighbouring nitro-groups in the course of the formation of the complex. Even in the presence of the electron-accepting substituent COOMe the appearance of an additional positive charge on the $C_{(1)}$ atom does not alter the general features of the addition process. As a result, when *sym*-TNB derivatives interact with acetone, the formation of σ-complexes of type (**XXI**) becomes preferred both kinetically and thermodynamically.

Table 3. The electronic and ^{1}H NMR spectra of type (**XXIVa**) complexes of *sym*-TNB and its derivatives[a].

X	Electronic spectra								^{1}H NMR spectra								
	λ_1, nm	lg ε_1	λ_2, nm	lg ε_2	λ_3, nm	lg ε_3	Solvent	Refs.	δ H^α (doublet)	δ H^β (triplet)	H^X	δ H^ε	δ H^η	$J_{\alpha,\beta}$	$J_{\beta,\varepsilon}$	Solvent	Refs.
H	572	4.267	464	4.569	—	—	Acetone	95, 92	8.45; 8.35	5.18; 5,08	—	—	—	1,0; 1,0	9.0; 5.5	[D_6]acetone [D_6]acetone	83 70, 111
H	560	—	465	—	—	—	Acetone	56	8,40; 8.31	5.20; 5.04	—	2.87; 2.61	2.63; 2,13	—	0.9; 5,5[b]	[D_6]acetone [D_6]acetone	83 84, 92
H	557	4.104	464	4,434	248	4.007	Methanol	84, 92	8.36	5,08	—	2,60	—	—	—	DMSO	83, 86, 88
H	560	4.076	460	4,408	—	—	Methanol	84	8.41	5.10	—	—	—	—	—	CH_3CN	83
CH_3	539	4.134	461	4,337	—	—	Acetone	56, 34 92, 30	8.47	5.20	2.51	2.46	2.13	—	6.0	[D_6]acetone	92
CH_3	536	—	461	—	242		Diglyme	92	—	—	—	—	—	—	—	—	—
OCH_3	534	4,134	444	4.403	—	—	Acetone	92, 89, 90	8.40	5.18	3.94	—	—	1.0	6.0	[D_6]acetone	89
OCH_3	520	4,086	445	4.335	246	3.882	Methanol	92	8.37	5.13	3.85	2.51	2.15	—	6.0	[D_6]acetone	92
OC_2H_5	510	—	445	—	—	—	Acetone	76	8.35	5.30	—	—	—	2.0	6.0	Acetone	70
OC_6H_5	—	—	—	—	—	—	—	—	8,50	5,20	—	—	—	2.0	6.0	Acetone	70
Cl	518	4.021	446	4,173	—	—	Acetone	92, 73	8,45	5.20	—	—	—	2,0	6.0	Acetone	70
Cl	505	4,100	450	4.230	258	4.072	Methanol	92	8.45	5.22	—	2.58	2,11	—	6.5	[D_6]acetone	92
$COOCH_3$	560	3.998	456	4,314	—	—	Acetone	92	8.37	5.12	3.60	2.56	2.15	—	6.0	[D_6]acetone	92
$COOCH_3$	550	3.987	456	4,297	250	3.975	Methanol	92	—	—	—	—	—	—	—	—	—
SCH_3	542	3.932	462	4,173	—	—	Acetone	92	8.33	5.34	2,32	2.46	2,14	—	6.5	Acetone	92
$COOC_2H_5$	555	—	450	—	—	—	Acetone	73	—	—	—	—	—	—	—	—	—
$N(CH_3)_2$	—	—	425	—	—	—	Acetone	73	8,37	5.35	—	—	—	1,0	7.0	Acetone	70
3,5-$(CH_3)_2$	590	3.77	480	3.919	—	—	Acetone	92	—	5.16	2,30	2.48	2.05	—	5.5	Acetone	92
3,5-$(CH_3)_2$	566	—	464	—	254	—	Diglyme	92	—	—	—	—	—	—	—	—	—
O^-	420	—	326	—	238	—	Water	100	8.74	4.99	—	2.86	2.25	—	6.0	D_2O	100

a) R = $CH_2^{\varepsilon}COCH_3^{\eta}$; b) $(CH_3)_3\overset{+}{N}H$ cation, $\delta(CH_3)_3$ = 2.85 p.p.m.

2,4,6-Trinitrobenzoic acid and its potassium salt undergo extremely rapid decarboxylation and it is possible to obtain[92] only the σ-complex (XXVIIIa) of *sym*-TNB and acetone. The study of the ultraviolet spectra of all the σ-complexes in methanol revealed a third maximum in the range 240–260 nm, which probably corresponds to the $\pi-\pi^*$ charge transfer within the cyclohexadiene system (Table 3).

Recent studies[93] of the infrared spectra of the σ-complexes of polynitro-compounds with acetone and alkoxides permitted an unambiguous assignment of the most intense bands in the range 1100–1300 cm^{-1} to the symmetrical stretching vibrations of the negatively charged nitro-group $[\nu_s(NO_2^-)]$. Moderately intense bands near 1500 cm^{-1} apparently correspond to the $\nu_{as}(NO_2^-)$ vibrations. Conclusions concerning the assignment of these bands to the ν_s and ν_{as} frequencies of the NO_2^- group have been confirmed[94] by polarisation Raman spectra.

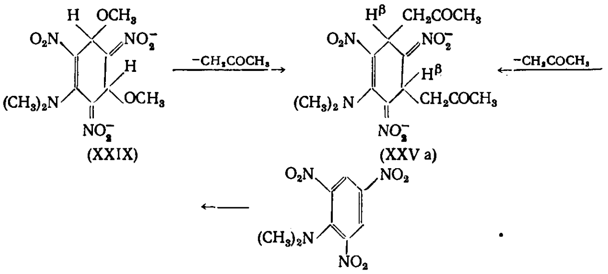
It has also been shown[95] that the Janovsky σ-complexes as well as the Meisenheimer complexes (XX) exhibit a fluorescence at reduced temperatures (77 K) characterised by a single long-wavelength band in the ranges 15 700–16 400 cm^{-1} [compound (XXVIIIa)] and 15 630–17 010 cm^{-1} [compound (VII)]; the intensity of the luminescence of the *sym*-TNB complex (XXVIIIa) is much higher and the spectrum of its polycrystalline form shows a splitting of the band into the two maxima.

The structure of the Janovsky σ-complex of *sym*-TNB (XXVIIIa) has also been demonstrated by X-ray diffraction studies[96], the results of which are presented in the Figure. It was shown that the ring is non-planar–the $C_{(1)}$ and $C_{(4)}$ atoms deviate from the plane of the $C_{(2)}$, $C_{(3)}$, $C_{(5)}$, and $C_{(6)}$ atoms by 0.30 and 0.11 Å respectively and are in the *cis*-position. The $C_{(1)}-C_{(2)}$ and $C_{(1)}-C_{(6)}$ bonds are single (1.54 Å), while the $C_{(2)}-C_{(3)}$ and $C_{(5)}-C_{(6)}$ bonds are predominantly double (see Figure), which demonstrates the overall quinonoid structure of this salt. The acetone residue is located in the plane perpendicular to that of the quinonoid part of the molecule. It is therefore more accurate to represent Janovsky σ-complexes by quinonoid structures of type (XXVIII) and (VII), despite the fact that in the majority of latest studies structures of type (XI) and (X) are quoted to take into account the delocalisation of the charge of the anion between the nitro-groups and the ring.

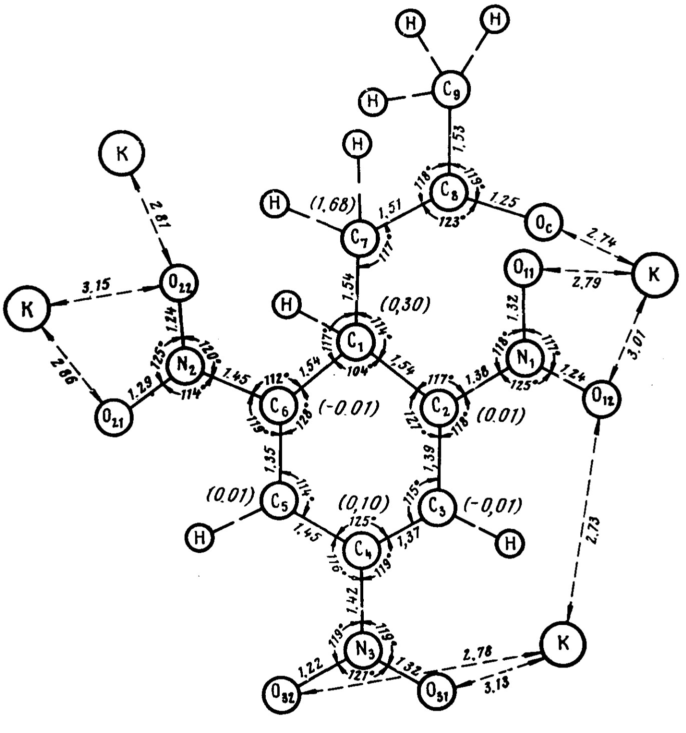
Thus application of the ^{1}H NMR method combined with electronic and infrared spectroscopic data as well as X-ray diffraction analysis finally established the structure of Janovsky complexes. They are products of the addition of acetone in the keto-form to an unsubstituted carbon atom of an aromatic ring with formation of a C–C bond; structures (IV), (V), (X), and (XI) are formed from *m*-DNB and its derivatives, while *sym*-TNB gives rise to structures (XXIV) and (XXVIII). The data obtained at the present time for the electronic and ^{1}H NMR spectra of these complexes are presented in Tables 1–3.

3. Multicharged Janovsky Complexes

In many cases the interaction of polynitro-compounds with acetone in an alkaline medium has been found to entail the formation of doubly and triply charged complexes, either as a result of the addition to the substrate of several acetone residues or as a result of the ionisation of substituents in the aromatic nitro-compound. Thus Foster et al. reported[70] that, when the σ-complex (XXIX) is dissolved in acetone, it is solvolysed with formation of the complex (XXVa, X = NMe$_2$), which is also formed when an acetone solution of *N,N*-dimethylpicramide is treated with a large excess of triethylamine. The product was identified by ^{1}H NMR (δH^β = 4.7 p.p.m.).



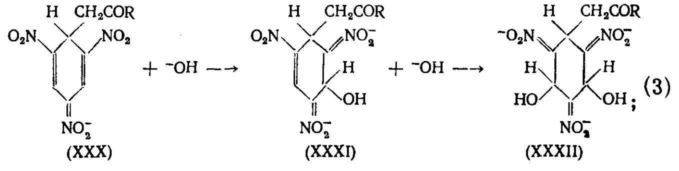
(2)



The geometry of the molecule of the σ-complex of *sym*-TNB with acetone (XXVIIIa). The distances (in Å) between the atoms of the anion and the $C_2C_3C_5C_6$ plane are given in brackets.

A dianionic complex of *sym*-TNB and acetone of type (XXV) was also obtained[97] in the presence of an excess of tetraethylammonium hydroxide. Its structure was demonstrated by electronic (λ_{max} = 516 nm) and infrared spectra [ν(C=O) = 1700 cm^{-1}, $\nu(NO_2^-)$ = 1110 cm^{-1}] as well as the splitting constants for the ESR spectrum of the radical-trianion obtained by its electrochemical reduction. It is suggested that this product has a non-planar structure.

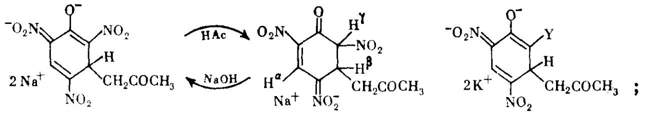
The first doubly charged mono-complexes of type (VI) were isolated a long time ago by Akatsuka[45,46]. In a series of studies[98-100] involving the investigation of the absorption spectra and of the structures of the acid decomposition products, a general mechanism was proposed for the reactions occurring following the addition of NaOH to solutions of the σ-complexes (XXXa) in water[98] and (XXXb) in dimethylformamide (DMF).[99]



(XXX) (XXXI) (XXXII) (3)

$R = CH_3$ (a) or C_6H_5 (b).

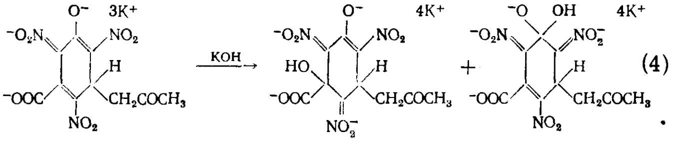
An analogous mechanism has been proposed for the conversion of the σ-complex of *sym*-TNB and cyclohexanone and a dianionic complex of type (XXXI) was isolated in a free form. The σ-complex (XXIVa) was subsequently obtained[100] (and identified) in similar reactions with picric acid. The complex is converted in an acid medium[101] into the complex (XXXIII), from which it can be regenerated by treatment with an excess of alkali.



(XXIVa) (XXXIII) (XXXIV)

$Y = COOCH_3$ (a) or COO^- (b).

On treating an acetone solution of 3,5-dinitrosalicylic acid with an alcoholic solution of KOH, Kovar[102-104] isolated the product (XXXIVb); the absorption spectrum of this complex is analogous to that of the corresponding methyl ester (XXXIVa), which was identified by ^{1}H NMR. The structure of the coloured crystalline σ-complexes (XXIVa) and (XXXVa), obtained similarly from picric and 3-hydroxy-2,4,6-trinitrobenzoic acids, was demonstrated by their chemical reactions and ^{1}H NMR. When one mole of 3-hydroxy-2,4,6-trinitrobenzoic acid is mixed with three moles of KOH in acetone, the σ-complex (XXXV) is formed; it was isolated in a free state and identified on the basis of its ^{1}H NMR and infrared spectra[104,105]. This product is converted into quadruply charged complexes (XXXVI) and (XXXVII) via the mechanism

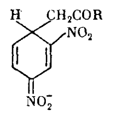


(XXXV) (XXXVI) (XXXVII) (4)

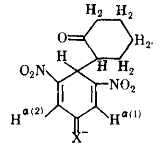
III. PRODUCTS OF THE ADDITION OF OTHER COMPOUNDS WITH MOBILE HYDROGEN ATOMS TO AROMATIC POLYNITRO-DERIVATIVES

By allowing *m*-DNB to interact with acetophenone in an alkaline medium, King and Newall[106] obtained a labile coloured product, whose decomposition with acid yields 2,4-dinitrobenzyl phenyl ketone, which indicates the addition of acetophenone in the keto-form to *m*-DNB. Pollitt and Saunders[44] showed that the characteristics of the formation of σ-complexes of types (IV) and (V) and of the blocking effect of substituents observed for acetone are largely retained in the reactions of *m*-DNB and its derivatives with cyclohexanone, diethyl malonate, cyclopentadiene, and di-n-butyl phosphite in DMF in the presence of NaOH. The relative yield of complexes of type (IV) then increases for cyclopentanone and cyclohexanone, while the reaction with di-n-butyl phosphite yields mainly complex (V). The σ-complexes of *m*-DNB and the ketones CH_3COR ($R = Me$, Et, n-Pr, n-Bu, iso-Bu, n-C_5H_{11}, and n-C_7H_{15}), obtained by Bronshtein et al.,[107] have been shown by correlation analysis of the oscillator strengths to be the addition products (XXXVIII). When ethyl methyl ketone was allowed to interact with *m*-DNB, 2,4-dinitroanisole, and *sym*-TNB in the presence of KOH, the σ-complexes (XXXVIII, $R = Et$), (IV, $X = OMe$, $R = CH_2COC_2H_5$), and (XXX, $R = Et$), in which the ketone residue is attached to an unsubstituted ring carbon atom, were isolated in a free state[108]. It has been shown by ^{1}H NMR[59] that the reaction of 3,5-dinitrobenzonitrile with diethyl ketone in DMSO in the presence of triethylamine leads to the formation of two isomeric σ-complexes of types (X) and (XI, $X = CN$) (Table 2).

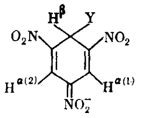
The products of the interaction of *sym*-TNB with various ketones have now been more fully investigated. The products of the addition of cyclohexanone to *sym*-TNB have been isolated[109] in the form of alkali and alkaline earth metal salts, for which the structure (XXXIX, $X = NO_2$) has been postulated.



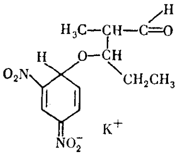
(XXXVIII)



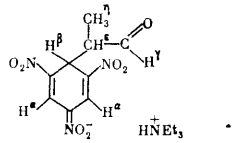
(XXXIX)



(XL)



(XLI)



(XLII)

Foster and Fyfe[84] investigated for the first time by ^{1}H NMR the products, obtained in a free form, of the interaction of *sym*-TNB with ethyl methyl ketone, diethyl ketone, and isopropyl methyl ketone in the presence of triethylamine. Elemental analysis and the electronic spectra correspond in all cases to type (XL) products of the addition of one ketone molecule to *sym*-TNB. The positions of the signals in the ^{1}H NMR spectrum, their relative intensities, and the spin–spin interaction constants in Table 4 established that compound (XLa) is formed in the case of diethyl ketone; only compound (XLb) has been isolated for isopropyl methyl ketone, while the reaction with ethyl methyl ketone results in the formation of both isomers, (XLc) and (XLd), in proportions of 4 : 1. In the study of acetonylacetone the authors were unable to isolate the σ-complex in a free form, while the study of ^{1}H NMR spectra in solution showed that the reaction entails the formation of a mixture of two isomers, (XLe) and (XLf), in proportions of 3 : 1. The splitting of the signals due to the $H^{\alpha(1)}$ and $H^{\alpha(2)}$ protons, caused by the asymmetry of the $C_{(1)}$ ring atom, has been observed[110] in the ^1H NMR spectra of a number of σ-complexes of *sym*-TNB with bulky substituents Y[compound (XL, g–j)] (Table 4). The authors believe that the temperature variation of the splitting confirms the view that it is due to the hindered rotation about the C–C bond between the rings in σ-complexes of type (XL). An analogous phenomenon has recently been observed[111] for the σ-complexes (XXXIX) of 1-X-3,5-dinitrobenzenes with cyclohexanone (Table 2).

Table 4. Electronic and ^1H NMR spectra of the σ-complexes of 1,3,5-trinitrobenzene with various nucleophiles containing a mobile hydrogen atom.

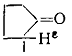
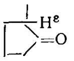
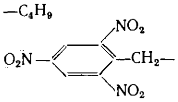
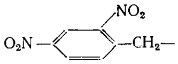
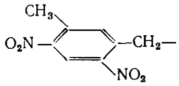
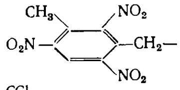
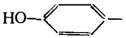
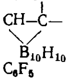
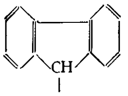
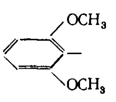
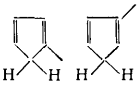
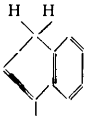
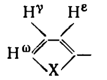
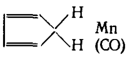
Structure	Y	Cation	Electronic spectra					^1H NMR spectra				Solvent^a	Refs.
			λ_1, nm	lg ε_1	λ_2, nm	lg ε_2	Solvent^a	δH^α	δH^β	$J_{\beta,\varepsilon}$	$J_{\alpha,\beta}$		
(XLa)	$CH_3CH_2COCH^eCH_3$	$H\overset{+}{N}Et_3$	550	4.09	465	4.40	M	8.45	5.31	3.0	1.0	DMSO	84, 110
(XLb)	$(CH_3)_2CH{-}COCH_2^e{-}$	$H\overset{+}{N}Et_3$	550	4.07	466	4.41	M	8.34	5.05	6.0	—	DMSO	84
(XLc)	$CH_3CH^eCOCH_3$	$H\overset{+}{N}Et_3$	—	—	—	—	—	8.46	5.35	3.0	—	DMSO	84
(XLd)	$CH_3CH_2COCH_2^e{-}$	$H\overset{+}{N}Et_3$	—	—	—	—	—	8.35	5.04	6.0	—	DMSO	84
(XLe)	$CH_3COCH_2CH_2COCH_2^e{-}$	$H\overset{+}{N}Et_3$	—	—	—	—	—	8.35	5.07	5.0	—	DMSO	84
(XLf)	$CH_3CO{-}CH^e{-}CH_2COCH_3$	$H\overset{+}{N}Et_3$	—	—	—	—	—	8.45	5.35	3.0	—	DMSO	84
(XLg)	$C_6H_5CH^eCOCH_2C_6H_5$	$H\overset{+}{N}Et_3$	—	—	—	—	—	8.4 (1); 8.3 (2)	5.74	3.0	1.0	DMSO	110 217
(XLh)	$C_6H_5CH^e{-}CN$	$H\overset{+}{N}Et_3$	—	—	—	—	—	8.32 (1); 8.21 (2)	5.47	3.5	1.0	DMSO	110
(XLi)		$H\overset{+}{N}Et_3$	—	—	—	—	—	8.37 (1); 8.30 (2)	5.01	0.7	1.0	DMSO	110
(XLj)		$H\overset{+}{N}Et_3$	—	—	—	—	—	8.33 (1); 8.21 (2)	5.33	—	2.5	DMSO	110
(XL)	$\overset{+}{P}(OEt)_3^b$	—	570	—	471	—	DMSO	8.53	5.45	—	2.5	DMSO	129
(XL)	$\overset{+}{P}(OMe)_3$	—	578	—	470	—	DMSO	8.50	5.44	—	2.5	DMSO	129
(XL)	$\overset{+}{P}(OEt_2)Ph$	—	591	—	481	—	DMSO	8.43	5.18	—	2.0	DMSO	129
(XL)	$\overset{+}{P}(NMe_2)_3$	—	599	—	486	—	DMSO	8.54	5.66	—	2.0	DMSO	129
(XL)	$NO_2CH_2{-}$	K^+	568	4.04	456	4.34	DMSO	8.41	5.35	—	7.5	DMSO	131
(XL)	CH_3CHNO_2	$H\overset{+}{N}Et_3$	552	4.08	452	4.38	DMSO	8.47	5.67	0.5	3.2	DMSO	131
(XL)	$(CH_3)_2C{-}NO_2$	$H\overset{+}{N}Et_3$	545	4.06	450	4.36	DMSO	8.51	5.90	1.4	0.0	DMSO	131
(XL)	$CH_3CH_2CHNO_2$	$H\overset{+}{N}Et_3$	552	4.04	452	4.34	DMSO	8.46	5.63	1.0	3.5	DMSO	131
(XXI)	$R{=}NO_2CH_2{-}^c$	$H\overset{+}{N}Et_3$	490	—	—	—	Al	8.40	5.77	5.0	1.0	DMSO	131
(XLIVa)	$CH_3SO{-}CH_2{-}$	K^+	518	—	440, 490^r	—	DMSO	8.34	6.83	—	—	[D$_6$]DMSO	136
(XL)	$(CH_3)_2NCO{-}$	K^+	510	—	440	—	DMSO	8.20	6.71	—	—	[D$_6$]DMSO	135
(XL)	$(CH_3)_2NCOCH_2{-}$	K^+	520	—	442	—	DMSO	—	—	—	—		136
(XL)	$CH_3C(CN)\overset{+}{N}Et_3$	—	560	—	447	—	DMSO	8.5; 8.4	5.00	—	2.0	[D$_6$]DMSO	138
(XL)	$-CH_3^{ee}$	$As^+(Ph)_4$	572	4.17	470	4.50	Al	8.24	4.64	6.2	0.75	[D$_3$]Al	149
(XL)	$-C_4H_9$	$\overset{+}{N}(CH_3)_4$	563	4.17	474	4.50	Al	8.39	4.84	4.2	0.75	[D$_3$]Al	149
(XL)		K^+	570	—	461	—	DMSO	8.31	5.17	6.0	—	[D$_6$]DMSO	153, 154
(XL)		K^+	570	—	462	—	DMSO	8.08	5.10	—	—	[D$_6$]DMSO	153
(XL)		K^+	568	—	468	—	DMSO	8.15	5.19	5.5	1.0	[D$_6$]DMSO	153, 154
(XL)		K^+	570	—	468	—	DMSO + M	8.15	5.09	5.5	—	[D$_6$]DMSO	153
(XL)	CCl_3	Na^+	495	—	427	—	E	8.61	6.35	—	—	[D$_6$]DMSO	155, 156
(XL)	CBr_3	Na^+	490	—	430	—	E	8.53	6.34	—	1.5	[D$_6$]DMSO	156
(XL)	CI_3	Na^+	—	—	—	—	—	8.48	5.69	—	1.5	[D$_6$]DMSO	156
(XXII)	$R{=}CH_3CO\bar{C}HCOOC_2H_5^f$	K^+	—	—	—	—	—	8.60	—	—	—	[D$_6$]DMSO	119
(XLIV)	$NO_2CH_2^g$	$H\overset{+}{N}Et_3$	562	—	—	—	Al + DMSO	8.30	4.18	—	—	Al + DMSO	131

Table 4 (Cont'd).

Structure	Y	Cation	Electronic spectra					^{1}H NMR spectra				Solvent[a]	Refs.
			λ_1, nm	lg ε_1	λ_2, nm	lg ε_2	Solvent[a]	δ H$^\alpha$	δ H$^\beta$	$J_{\beta,\varepsilon}$	$J_{\alpha,\beta}$		
(XL)	H	$\overset{+}{N}(CH_3)_4$	585	4.18	478	4.49	Al	8.26	3.88	—	0.5	Al	143
(XLVII)	H^s	$\overset{+}{N}(CH_3)_4$	550	4.53	478	4.44	Al	8.24	3.87	—	—	[D$_6$]DMSO	145
(L a)	H	$\overset{+}{N}(CH_3)_4$	—	—	—	—	—	8.35	4.04	—	—	[D$_6$]DMSO	145
(L b)	H^i	$\overset{+}{N}(CH_3)_4$	—	—	—	—	—	8.35	3.92	—	—	[D$_6$]DMSO	145
(L c)	H^j	$\overset{+}{N}(CH_3)_4$	580	4.53	478	4.40	Al	8.38	3.90	—	—	[D$_6$]DMSO	145
(XL d)		K$^+$	570	—	468	—	DMSO + M	8.44	5.62	—	—	[D$_6$]DMSO	157
(XL)	$C_6H_5CH^e-CO_2C_2H_5$	Na$^+$	—	—	—	—	—	8.30	5.67	4,6	2.1	[D$_6$]DMSO	87
(XL)		Na$^+$	—	—	—	—	—	8.48	5.90	—	—	[D$_6$]DMSO	87
(XL)	C_6F_5	Na$^+$	—	—	—	—	—	8.48	6.10	—	—	[D$_6$]DMSO	87, 88
(XL)	$(CF_3)_2CH-$	Na$^+$	—	—	—	—	—	8.46	5.58	—	—	[D$_6$]DMSO	87
(XL)	CN	Na$^+$	—	—	—	—	—	8.40	5.70	—	—	[D$_6$]DMSO	87
(XL)		$\overset{+}{Sn}(CH_3)_3$	—	—	—	—	—	8.50	5.80	—	—	DMSO	88
(XLm)		$\overset{+}{Py}H$	585	4.75	475	4.43	P	8.35	6.32	—	0.2	[D$_6$]DMSO	160
			—	—	—	—	—	8.21	6.53	—	1 3	[D$_6$]Al	160
			—	—	—	—	—	8.12	6.44	—	1.3	[D$_6$]D	160
(XL)		$\overset{+}{Py}H$	520	—	437	—	P	8.82 & 8.79	5.59 & 5.88	—	—	[D$_5$]P	163
								8.40	5.62	—	—	[D$_6$]DMSO	163
								8,55	5.75	—	—	[D$_6$]An	163
(XLi)		$\overset{+}{Py}H$	580	4,18	475	4.48	P	8,90	6.14	—	—	[D$_5$]P	163
								8.86	6.08	—	—	[D$_6$]An	163
(XL)	 X=O^k	$\overset{+}{Py}H$	—	—	—	—	—	8,73	5,86	—	<0,3	[D$_6$]DMSO	164
(XL)	X=S^l	$\overset{+}{Py}H$	558	4,18	454	4,48	An	8,73	6.00	—	<0,3	[D$_6$]DMSO	164
(XLo)		$\overset{+}{Py}H$	550	—	460	—	P	8.45	5 65	—	—	DMSO	165

a) M = methanol, DMSO = dimethyl sulphoxide, Al = acetonitrile, E = ethanol, An = acetone, P = pyridine, D = dioxan; b) $J_{\alpha,P}$ = 21 Hz, $\delta(CH_2)$ = 4.5 p.p.m., $\delta(CH_3)$ = 1.53 p.p.m.; c) X = $N(CH_3)_2$; d) inflection; e) $\delta(CH_3)$ = 1.14 p.p.m.; f) X = OCH_3, δH = 3.4 p.p.m.; δ = 3.8(2H), 2.2(3H), and 1.1(3H) for R; g) R = H$^\gamma$, δH$^\gamma$ = 5.38 p.p.m., δH$^\omega$ = 6.59 p.p.m.; $J_{\omega,\gamma}$ = 10.2 Hz, $J_{\alpha,\gamma}$ = 1.9 Hz, $J_{\beta,\omega}$ = 5.0 Hz; h) λ_3 = 262 nm, lgε_3 = 4.18, $\delta[\overset{+}{N}(CH_3)_4]$ = 3.12 p.p.m.; i) $\delta(OCH_3)$ = 3.76 p.p.m.; j) λ_3 = 256 nm, lgε = 4.04, $\delta(CH_3)$ = 2.58 p.p.m.; k) $J_{\varepsilon,\gamma}$ = 6.6 Hz, $J_{\varepsilon,\omega}$ = 0.8 Hz, $J_{\gamma,\omega}$ = 1.18 Hz; l) $J_{\varepsilon,\gamma}$ = 6.4 Hz, $J_{\varepsilon,\omega}$ = 1.1 Hz, $J_{\gamma,\omega}$ = 5.3 Hz.

Thus the Janovsky reaction with various ketones exhibits the characteristics described above for acetone. Furthermore, in many instances isomers are formed due to the presence of several reaction centres in complex ketones. The non-equivalence of the $H^{\alpha(1)}$ and $H^{\alpha(2)}$ protons has been observed for ketones with bulky substituents.

Very much less attention has been devoted to the interaction of polynitro-compounds with aldehydes. A spectrophotometric study of this reaction for a series of aldehydes showed[112] that the first stage is aldol condensation of the aldehydes, after which the polynitro-compound combines with the aldol alkoxide to form a σ-complex of type (XLI). Having isolated the product of the interaction of propionaldehyde with *m*-DNB, Gitis and Kaminskii[113] concluded somewhat later that this involves the addition of the aldol—the product of the condensation of four molecules of the initial aldehyde—to *m*-DNB. After treating *sym*-TNB with triethylamine in propionaldehyde, Strauss[114] isolated a crystalline product, to which he proposed structure (XLII) on the basis of elemental analysis and infrared [ν(C=O) = 1720 cm^{-1}] and visible (λ_{max} = 470 and 566 nm in methanol) spectra. This structure was also confirmed by the ^{1}H NMR spectrum. Thus in this case the aldehyde reacts like ketones, which may be due, on the one hand, to the greater reactivity of *sym*-TNB compared with *m*-DNB and, on the other, to the smaller capacity of diethylamine (compared with KOH) to induce aldol condensation.

The interaction of *m*-DNB with ethyl malonate, phenylacetate, and cyanoacetate in the presence of aqueous KOH yielded coloured solutions whose absorption maxima are in the same part of the spectrum as for the products of the reaction with acetone (515 ± 15 nm). On this basis, the authors[23-25,31] believe that the structures of the complexes are the same in all cases.

However, there are few reliable data on the structures of such products. In an early study Jackson and Gazzolo[115] isolated the products of the addition of the sodium derivatives of malonic and acetoacetic esters to *sym*-TNB and 2,4,6-trinitroanisole in proportions of 3 : 1. Their insignificant stability indicates, according to the authors, an addition reaction with formation of a C–O bond and not a C–C bond. The products of the addition of two molecules of sodium derivatives of acetophenone, benzyl cyanide, and malonic and cyanoacetic esters to *m*-DNB have been obtained[14]. Shein and Ivanova[116] showed that the σ-complex isolated by Baudet[117] in the reaction of equivalent amounts of 1-fluoro-2,4-dinitrobenzene with malonic ester in the presence of triethylamine is a mixture of the initial 1-fluoro-2,4-dinitrobenzene, diethyl 2,4-dinitrophenylmalonate, and ethyl α,α-bis(2,4-dinitrophenyl)acetate. By treating[118] 9-nitroanthracene with the sodium derivatives of malonic ester, methylmalonic ester, nitropropane, etc. in DMSO, intensely coloured solutions, evidently containing the σ-complexes [XVIIb, Y = $CH(CO_2Et)_2$, $C(CH_3)(CO_2Et)_2$, $C(CH_3)_2NO_2$, $CH(CN)_2$, etc.], were obtained; after acidification, they are converted quantitatively into the corresponding derivatives of dihydroanthracene.

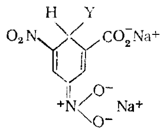
The only study where the structure of coloured products of this type was demonstrated unambiguously is that of Strauss[119], who treated a tetrahydrofuran solution of 2,4,6-trinitroanisole with an excess of acetoacetic ester in the presence of potassium butoxide and isolated the 1 : 1 adduct [XXII, X = OMe, R = $CH(COCH_3)COOEt$]. Its structure was established by elemental analysis and ^1H NMR (Table 4); on treatment with an acid, the OMe group is split off and ethyl α-picrylacetoacetate is formed.

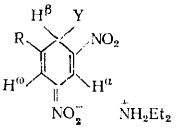
After surveying the entire data accumulated at the time, Foster and Mackie[37] concluded, following Canbäck[23-25], that not only carbonyl compounds but also many other substances with a fairly mobile hydrogen atom can react successfully with polynitro-compounds. Indeed, instances of the employment of uric acid and a number of amino-acids[18], laevulose, glucose, and other sugars[22,23], instead of acetone, in the colour reaction have been described. On the other hand, if the ion of the conjugate base is extremely stable, no colour is produced[37]. Many dialkyl and alkyl aryl ketones and derivatives of fluorene, indene, phenanthrene, etc. give rise to an intense violet colour on reaction with o-dinitrobenzene or 2,2′-dinitrobiphenyl in DMF in the presence of tetrabutylammonium hydroxide[120-123]. In many instances a colour appears on interaction of *m*-DNB and its derivatives with DMF in the presence of alkali[121,124].

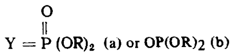
Numerous studies have been made on the interaction of *sym*-TNB and *m*-DNB with compounds having a mobile hydrogen atom. Saunders and Stark[125] suggested that coloured products (XLIIIa) or (XLIIIb) are formed in the reaction of 3,5-dinitrobenzoic with dialkyl phosphites. Alkylphosphine oxides in the presence of 30% NaOH[126], methylenediphosphonates[125], di-isopropyl ethynylphosphonate[127], alkyltriphenylphosphonium salts[120], and quaternary α- and γ-picolinium salts[128] give rise to a similar colour reaction. It has been shown recently[129] that trialkyl phosphites, phosphorimidites, phosphonites, phosphinites, and dialkyl phosphorofluoridites (but not triphenyl phosphite) react readily with *sym*-TNB in DMSO to form σ-complexes of type (XL), which are converted in solution into the corresponding phosphoryl compounds ($Ar\overset{+}{P}OR'R''$). Some of the σ-complexes [XL, Y = $\overset{+}{P}(OMe)_3$, $\overset{+}{P}(OEt)_3$, $\overset{+}{P}(OEt)_2Ph$, or $\overset{+}{P}(NMe_2)_3$] have been identified with the aid of ^1H NMR and electronic spectra (Table 4). It is believed[129] that phosphorylation of *sym*-TNB and its halogeno-derivatives by phosphorus(III) compounds proceeds via the intermediate formation of σ-complexes of type (XXII, X = H, F, or Cl, R = $\overset{+}{P}R_3$), whose stability is to a large extent determined by the ease of elimination of the substituted group and by the nature of the solvent.

Urbanskii[130] was the first to measure the absorption spectra of the products of the reaction of nitromethane and other nitroalkanes with *m*-DNB and *sym*-TNB in methanol in the presence of NaOH. Subsequently treatment with triethylamine led to the isolation[131] in a free form of σ-complexes of type (XL) after the reaction of *sym*-TNB and *N*,*N*-dimethyl-2,4,6-trinitroaniline with a series of nitroalkanes (Table 4). Their electronic and ^1H NMR spectra are close to the characteristics of the corresponding acetone complexes (Table 3) as well as the σ-complex of *m*-DNB and nitromethane (XLIV, R = H, Y = CH_2NO_2), which has been investigated in solution (Table 4). Furthermore, the formation in reaction solutions of σ-complexes of nitromethane with 1,3-dinitronaphthalene (XVIb) and with 3,5-dinitropyridine has been detected with the aid of electronic and ^1H NMR spectra[131]; in the latter case a mixture of isomers analogous to (XIIIb) and (XIV) is formed.

A study of the reaction of *m*-DNB and a series of 1-R-3,5-dinitrobenzenes (R = H, $CONH_2$, CO_2Et, CO_2Na, etc.) with DMSO led to the conclusion[132,133] that the coloured products have a structure analogous to that of the products of the reaction with acetone and that DMSO may add in the "keto-form" (XLIVa) or in the "enolic" form (XLIVb). In the interaction of $-CH_2SOCH_3$ with *sym*-TNB in DMSO Foster and coworkers[134,135] detected by ^1H NMR the σ-complex (XLIVa) (Table 4), which, however, is rapidly converted into (XXIII, X = H). Soon the σ-complex (XLIVa) was isolated in a free form[136] and its structure was demonstrated; the stretching vibration of the S=O bond is observed in the infrared spectra at 1035 cm⁻¹ and that of the $S-CH_3$ groups occurs at 1320 and 1410 cm⁻¹. The same workers[146] isolated type (XL) products of the interaction of *sym*-TNB with DMF or dimethylacetamide, a detailed study of which showed (Table 4) that the addition of a nucleophile takes place also with formation of a C–C bond. It was noted that in acetone and acetonitrile the added DMSO, DMF, etc. anions are displaced by the more active anions $-CH_2CN$ and $-CH_2COCH_3$. Certain products of the addition of CH_3CN to polynitro-compounds, namely σ-complexes of type (XXI, X = H or COOH, R = CH_2CN) as well as (IV) and (V) with X = H or OMe and R = CH_2CN (Table 2) were investigated recently[137] with the aid of electronic, ^1H NMR, and infrared spectra. As in the reactions with acetone and nitromethane, the addition of acetonitrile leads to the formation of a C–C linkage.

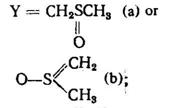






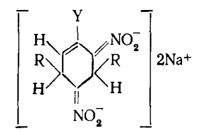
$Y = \overset{O}{\overset{\|}{P}}(OR)_2$ (a) or $OP(OR)_2$ (b)

(XLIII)



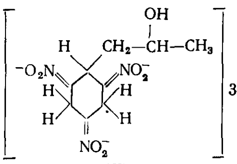
$Y = CH_2SCH_3$ (a) or $\overset{O}{\overset{\|}{}}\!-\!S(CH_2)(CH_3)$ (b);

(XLIV)



R = H (a) or Alk (b).

(XLV)

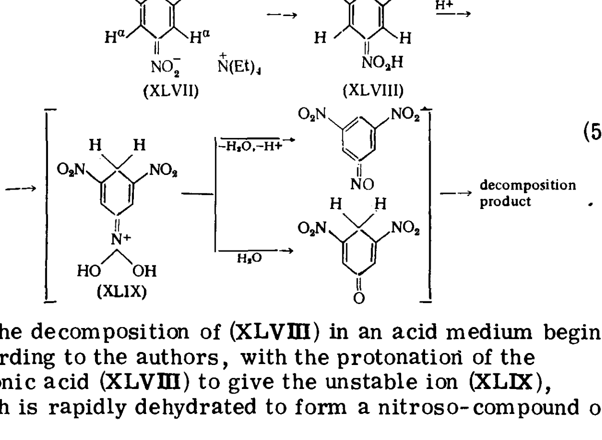


(XLVI)

When a solution of *sym*-TNB in acrylonitrile was treated with triethylamine, an extremely unstable 1 : 1 : 1 addition product was isolated[138] after subsequent precipitation with ether. Having analysed its ^{1}H NMR spectra, the authors gave preference to the second of the two possible structures of the zwitter-ions [XL, Y = $-CH(CN)CH_2\overset{+}{N}Et_3$] and [XL, Y = $-C(CH_3)(CN)\overset{+}{N}Et_3$] (Table 4).

In a study of the reduction of *m*-DNB, *sym*-TNB, and its derivatives with sodium tetrahydroborate to the corresponding polynitrocyclohexanes Severin and coworkers[139, 140] suggested the formation of intermediates involving the addition of one (IV or V, R = H, X = H, Cl, Br, Me, COOH, or CH = CHC_6H_5) and then two (XLVa) and three (XXVI, R = H) hydride ions to the initial nitro-compounds. Certain products of type (XLV) were obtained in the form of crystalline salts[141], which proved to be stable in the case of 2,4- and 3,5-dinitroanisoles and labile in the case of *m*-DNB. The structure of the complexes (XLV, Y = OMe, R = H) was demonstrated by their conversion into azabicyclononene derivatives as a result of aminoalkylation. The possibility of the formation of the trianionic complex (XLVI) after the reduction of the σ-complex (XXVIIIa) derived from *sym*-TNB with sodium tetrahydroborate was demonstrated[142]. Although the product (XLVI) was not isolated in a free form, its structure was confirmed by the finding that, on being oxidised with bromine, it is converted into 2-methyl-4,6-dinitrocoumaran.

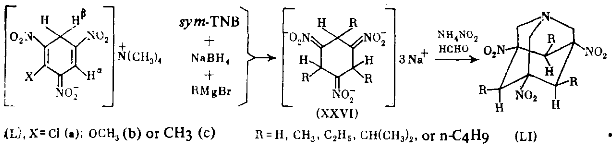
When *sym*-TNB was mixed with tetraethylammonium tetrahydroborate in acetonitrile in an atmosphere of nitrogen, purple crystals of the σ-complex (XLVII) were isolated[143]. Treatment of this complex with sulphuric acid made it possible to obtain[144] the nitronic acid (XLVIII), which is stable only in dilute solutions. Its absorption maximum in chloroform is at 370 nm, while in ethanol two maxima, characteristic of the usual σ-complexes of type (XXVIII), are observed.



(5)

The decomposition of (XLVIII) in an acid medium begins, according to the authors, with the protonation of the nitronic acid (XLVIII) to give the unstable ion (XLIX), which is rapidly dehydrated to form a nitroso-compound or is hydrolysed to cyclohexadienone. To confirm this mechanism, the authors isolated and demonstrated the structures of the decomposition products [3,5-dinitroaniline, *N*-(3,5-dinitrophenyl)hydroxylamine, 3,3′,5,5′-tetranitroazoxybenzene, 3,3′,5,5′-tetranitrohydrazobenzene, bis-(3,5-dinitrophenyl)amine, and 3,5-dinitrophenol]. The hydride complex (XLVII) was also isolated[145] after treating an acetonitrile solution of *sym*-TNB with tetramethylammonium octahydroborate in an inert atmosphere. The hydride complexes of 1-X-2,4,6-trinitrobenzenes (L) were obtained similarly[145]; when X = Cl or OMe, the complexes are isolated in a mixture with (XLVII), the complex (L) being obtained in a pure form only for X = Me†.

The interaction of *sym*-TNB and *m*-DNB with Grignard compounds in the presence of sodium tetrahydroborate, which results in the formation of 1,3,5-trialkyl-2,4,6-trinitrocyclohexanes and dialkyldinitrocyclohexanes respectively, proceeds, according to Severin and coworkers[146,147], via intermediate complexes of type (XLV) and (XXVI) with R = Me, Et, etc. The authors were unable to isolate these products and to investigate their structures, while aminomethylation of (XLVI, R = Me) and (XXVI, R = Me) by formaldehyde and ammonium nitrate makes it possible to obtain[148] a series of trinitroaza-adamantanes (LI), whose structure has been convincingly demonstrated by a number of methods.



(6)

(L), X = Cl (a); OCH_3 (b) or CH_3 (c) R = H, CH_3, C_2H_5, $CH(CH_3)_2$, or n-C_4H_9 (LI) .

The products of the addition of aliphatic and aromatic hydrocarbons, with fairly mobile hydrogen atoms, to *sym*-TNB were obtained by a number of workers, who either used specific reagents or selected appropriate reaction conditions. Thus, on treating *sym*-TNB in acetone and in an inert atmosphere with tetramethylammonium (or tetraphenylarsonium) tetra-alkylborates, Taylor[149] obtained the σ-complexes (XL, Y = Me or Bu) (Table 4).

Electrochemical reduction of *sym*-TNB in acetone at a controlled potential, corresponding to the transfer of two electrons, led to the isolation[150] of the "paired" σ-complex (LII)—the product of the interaction of two *sym*-TNB molecules with one another—which has two absorption maxima (at 432 and 510 nm), characteristic of σ-complexes of type (XXVIII). Its ^{1}H NMR spectrum has only two singlets—due to the four H^α protons (δ = 8.01 p.p.m.) and two H^β protons (δ = 5.37 p.p.m.); its infrared spectrum is analogous to that of (XXVIIIa), but there is no ν(C=O) band.

Foster and Mackie[37] observed that solutions of 2,4-dinitrotoluene in alkaline ethanol absorb at ~ 520 nm, which they attributed to the complex (LIII, Y = H). Here 2,4-dinitrotoluene behaves both as an electron acceptor and as a substance with mobile hydrogen atoms. On the other

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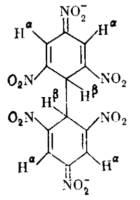
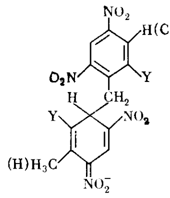
† It has been shown recently[218] that hydride σ-complexes of type (XLVII) can be readily isolated after the interaction of *sym*-TNB with dihydro-derivatives of nitrogen-containing heterocycles: 1,3-dimethylbenzimidazoline, 1,3-dimethylnaphtho[2,3-*d*]imidazoline, 1,3-dimethyl-2,3-dihydropyrimidine, and 1-benzyl-1,4-dihydronicotinamide. A σ-complex of *sym*-TNB with the model coenzyme NADH was also detected, which may be important in biochemistry for the investigation of the mechanism of oxidation-reduction reactions.

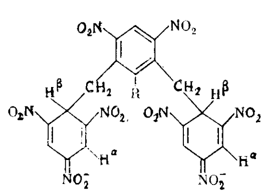
hand, Pollitt and Saunders[44] believe that the long-wavelength maximum (at 648 nm), arising when a solution of 2,4-dinitrotoluene in DMF is treated with NaOH, corresponds to the 2,4-dinitrobenzyl anion and not the complex (**LIII**, Y = H). This is confirmed by the results of quantum-chemical calculations[151] of its structure and electronic spectra. A study of the kinetics of the rapid reaction of 2,4,6-trinitrotoluene with alkoxides in an alcoholic medium demonstrated the possibility of the formation of the products (LIII, Y = NO_2) with calculated absorption maxima at ~ 450 and ~ 550 nm. However, a compound of this type could not be isolated in a free form and it was investigated in detail much later[153,154]. When 2,4,6-trinitrotoluene is added to a solution of *sym*-TNB in DMSO in the presence of KOH, new maxima, corresponding to the σ-complex [XL, Y = 2,4,6-$(NO_2)_3C_6H_2CH_2$], appear at 465 and 580 nm, instead of the absorption spectrum of the σ-complex with the OH^- ion (**XXIII**, X = H) formed initially (λ_{max} = 440 and 518 nm).



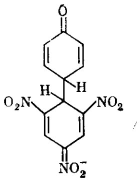
(LII)



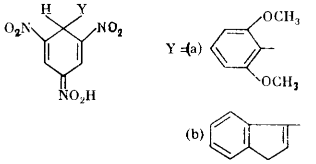
(LIII), Y = H, NO_2



R = NO_2 (a); H (b)
(LIV)



(LV)



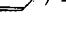
(LVI)

σ-Complexes of *sym*-TNB with 2,4-dinitrotoluene, 4,6-dinitro-*m*-xylene, and 2,4,6-trinitro-*m*-xylene were obtained similarly (Table 4). In the last two cases treatment with alkali in a polar medium may result in the ionisation of the second methyl group, which entails the formation of the σ-complexes (LIV, a and b) in the interaction with *sym*-TNB. These compounds were also isolated in a free form and identified with the aid of electronic and ^1H NMR spectra. Electronic absorption spectra make it possible to detect similar reactions with *sym*-TNB and other alkyl derivatives of *m*-DNB or *p*-nitrotoluene[154]. Thus it has been established that, under the influence of alkali in aprotic solvents, *sym*-TNB and *m*-DNB derivatives containing methyl groups may behave not only as electron acceptors but also as nucleophiles as a result of the dissociation of a hydrogen atom in the methyl group.

Shein and coworkers[155,156] showed by ^1H NMR that, when the σ-complex of *sym*-TNB with potassium methoxide (XX, Y = NO_2, X = OMe) is treated with haloforms in DMSO in the presence of NaOMe, the stable σ-complexes (XL, Y = CCl_3, CBr_3, or CI_3) are formed, and isolated the first two in a free form (Table 4). Similar reactions occur when weaker bases are used: piperidine, diethylamine, and triethylamine. An interesting case of the formation of a σ-complex with a C–C and not a C–O bond has been described[157]. In accordance with the ambident nature of the phenoxide ion, its slow interaction with *sym*-TNB in a 4 : 1 DMSO–MeOH mixture leads to the σ-complex (LV), which then rearranges to (XLk, Y = *p*-HOC_6H_4). The latter was isolated in a free form (Table 4) and proved to be fairly stable even in weakly acid media.

The use of organometallic compounds as a source of carbanions is of considerable interest. A very novel method has been proposed by Beletskaya and coworkers[86,87], who treated *sym*-TNB with a series of organomercury compounds of the type R_2Hg and RHgX in DMSO in the presence of NaI and obtained a series of new σ-complexes [XL, Y = CHPhCOOEt, $B_{10}H_{10}C_2H$, C_6F_5, $(CF_3)_2CH$, CN, or CCl_3, X = Br], which were identified by ^1H NMR in the reaction solutions (Table 4). σ-Complexes of type (XL) were obtained similarly[88] by employing organotin compounds $RSnMe_3$ (where R = C_6F_5, fluorenyl, cyclopentadienyl, or indenyl, but not alkyl or phenyl) (Table 4). In certain cases a mixture of isomers is formed, for which a complete analysis of ^1H NMR spectra is difficult. The same workers recently synthesised[158] σ-complexes of a new type in which the tetrahedral carbon atom is linked to Si, Ge, and Sn. The compounds R_2EM (R_2E = Me_3Sn, Ar_3Sn, Et_3Ge, or Me_3Si, M = K or Li) were added to a solution of *sym*-TNB in tetrahydrofuran at temperatures down to −30°C in an inert atmosphere. All the σ-complexes obtained have characteristic electronic spectra (λ_1 = 435–440 nm, and λ_2 = 494–500 nm) and ^1H NMR spectra (δH^α = 8.30–8.40 p.p.m., δH^β = 6.10–6.30 p.p.m., 2 : 1 ratio), which confirms their structure. On treatment with acetone, they are converted into the corresponding Janovsky σ-complex (XXVIII).

Wennerström and coworkers[159] showed that, when phenylcopper reacts with *sym*-TNB in pyridine or quinoline at room temperature, an intensely coloured compound is formed. They identified it as a σ-complex on the basis of the characteristic absorption in the visible spectrum (λ_{max} = 444 and 522 nm). For the more stable 2,6-dimethoxyphenylcopper, it was possible to obtain a fairly stable crystalline complex (XLl), which was isolated as the pyridinium salt after acidifying the reaction mass with acetic acid (Table 4). Similar reactions occur, albeit more slowly, with 2,4,6-trimethoxy- and 2,6-dimethoxyphenyl silver[160]. In the latter case acidification of the σ-complex (XLl) with dilute H_2SO_4 made it possible to isolate in a free form 4-(2,6-dimethoxyphenyl)-3,5-dinitrocyclohexa-2,5-dienenitronic acid (LVIa). Its structure was demonstrated with the aid of infrared and ^1H NMR spectra; the ^1H NMR spectrum in DMSO virtually coincides with the spectrum of the corresponding σ-complex (XLl). In a polar medium (pyridine, ethanol) the nitronic acid fully dissociates with formation of the anion (λ_{max} = 470 and 590 nm), in a non-polar medium ($CHCl_3$) the undissociated form predominates (λ_{max} = 360 nm), while in acetone the two forms are in equilibrium and the spectrum shows all three maxima. Analogous results were obtained[161] in a study of the interaction of *sym*-TNB in pyridine with phenylethynylcopper and phenylethenylsilver and with hexylcopper. The formation of coloured σ-complexes (XL, Y = C≡C–Ar) was detected with the aid of electronic spectra (λ_{max} = 442 and 530 nm) and confirmed by the structure of the acid decomposition products isolated, among which the main component is 2,4,6-trinitrotolane.

The interaction of *sym*-TNB with cyclopentadiene[162,163] in pyridine in the presence of silver oxide leads to two isomeric σ-complexes (XL, Y = 1,3- or 1,4-cyclopentadienyl) in approximately equal amounts (Table 4). When *sym*-TNB is acted upon by indene under analogous conditions, the σ-complex with pyridine (XL, Y = ) is formed initially (λ_{max} = 437 and 520 nm) and is then gradually converted into the σ-complex (XLm), which has been isolated in 87% yield and identified (Table 4). On treatment with H_2SO_4, this complex is converted into 4-(3-indenyl)-3,5-dinitrocyclohexa-2,5-dienenitronic acid (LVIb), which is reconverted under the influence of NaOH into the "indenyl" σ-complex (XLm). The σ-complexes of *sym*-TNB with 2-furyl-, and 2-thienyl-copper (Table 4) have been isolated in a free form at a reduced temperature[164]. The reaction of *sym*-TNB with cyclopentadienylmanganese silver tricarbonyl in pyridine similarly leads to the formation[165] of the corresponding σ-complex (XLn) (Table 4).

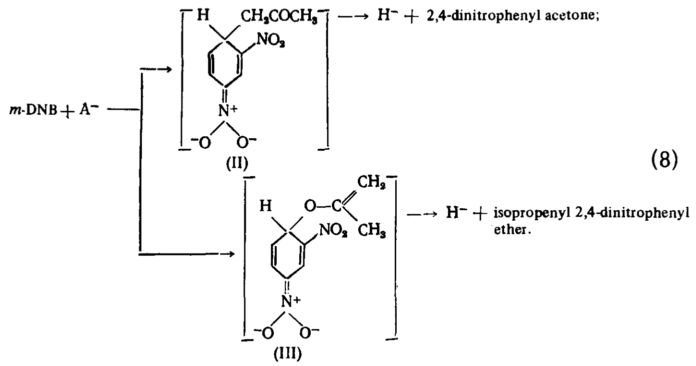
Thus the interaction of polynitro-derivatives of aromatic hydrocarbons with various compounds containing mobile hydrogen atoms yields Janovsky σ-complexes in an alkaline medium, in which a C–C bond is formed between a tetrahedral ring carbon atom and a carbon atom of the nucleophile. Under these conditions, their further reduction or acid decomposition in many instances lead to new pathways towards the formation of previously unobtainable aromatic and alicyclic compounds.

IV. KINETICS AND MECHANISM OF THE JANOVSKY REACTION

1. The Formation of σ-Complexes

In his review Canbäck[166] examined the mechanisms proposed[14,15,36] for the Janovsky reaction and showed that none is sufficiently convincing. He suggested for the first time[23] that the interaction of *m*-DNB with acetone in an alkaline medium be regarded as nucleophilic substitution of a hydrogen atom in the aromatic ring by the acetone residue in one of its tautomeric forms [Eqn. (7)] with formation of 2,4-dinitrophenylacetone or isopropenyl 2,4-dinitrophenyl ether [(Eqn. (8)]:

$$CH_3COCH_3 + {}^-OH \rightleftarrows [\underbrace{CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-\bar{C}H_2 \leftrightarrow CH_3-\overset{\overset{\displaystyle O^-}{|}}{C}=CH_2}_{(A^-)}] + H_2O \qquad (7)$$

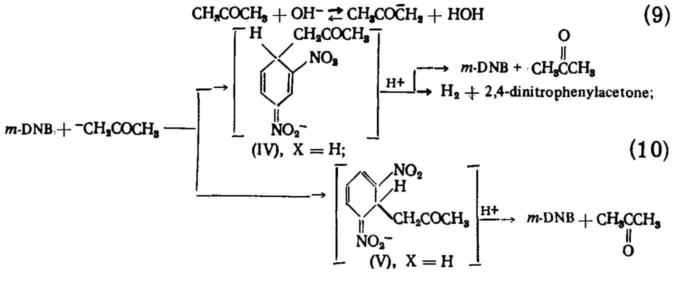


(8)

However, all attempts to isolate the final reaction product proved to be unsuccessful.

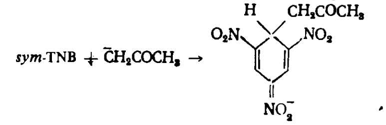
In a number of studies[23,26,120,166] dealing with the mechanism of the Janovsky reaction an analogy is drawn with the mechanism of the formation of type (XX) Meisenheimer σ-complexes[1,6]. In their survey of these ideas, Gitis and Kaninskii[48,50] proposed a mechanism for the formation of Janovsky reaction products and their decomposition in an acid medium:

$$CH_3COCH_3 + OH^- \rightleftarrows CH_2CO\bar{C}H_3 + HOH \qquad (9)$$



It is based on the observation that the acetone residue adds in the keto-form to polynitro-compounds[50] and on the identification of the above decomposition products[48,50]; it may be regarded as the first general mechanism of the Janovsky reaction supported by experimental data. These ideas were confirmed by Foster and Fyfe[84], who, having obtained the Janovsky σ-complex by the interaction of *sym*-TNB with acetone in the presence of tertiary amines, assumed that the amine reacts as a base, after which *sym*-TNB is attacked by the acetone carbanion

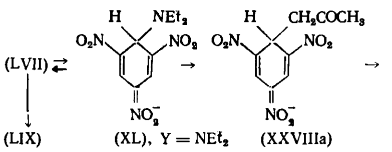
$$NEt_3 + CH_3COCH_3 \rightleftarrows \overset{+}{N}HEt_3 + \bar{C}H_2COCH_3 \qquad (11)$$



(XXVIIIa) (12)

However, the same workers showed[85] that in the presence of diethylamine (DEA) the above reaction proceeds via a more complex pathway. After the addition of DEA to an acetone solution of *sym*-TNB, ^1H NMR spectra revealed the successive formation of (XL, Y = NEt_2) and then (XXVIIIa), which are converted after a long time into a 1 : 1 mixture of *N*,*N*-diethyl-4-nitroaniline and an aliphatic dinitro-ketone (LVIII). It was established that these compounds are formed directly from (XXVIIIa) in acetone and, when deuterated acetone was used, *N*,*N*-diethyl-4-nitro-[2,6-D]aniline was obtained. A cyclic complex (LIX), which the authors believe is formed either directly from *sym*-TNB or from (LVII) but not via (XXVIIIa), was also isolated from the reaction mixture. On this basis, the authors[85] proposed a general reaction mechanism, which, however, did not receive further experimental confirmation or theoretical justification:

$$sym\text{-TNB} + 2NHEt_2 \rightleftarrows \text{(LVII) (charge-transfer complex)}, \qquad (13)$$



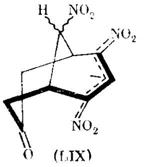
$$\rightarrow N,N\text{-diethyl-}p\text{-nitroaniline} + \underset{\text{(LVIII)}}{CH_3COCH_2-CH(CH_2NO_2)_2}\ . \qquad (14)$$

Studies on the kinetics of the reactions of polynitro-compounds with ketones in an alkaline medium have been published comparatively recently. Caldin and coworkers[167] investigated for the first time by the stopped flow method the kinetics of the reaction of *sym*-TNB with DEA in acetone at low temperatures (down to −85°C). In order to account for the observed third order of the reaction (first with respect to *sym*-TNB and second with respect to DEA), they suggested that equilibrium is established rapidly initially, possibly involving the dimerisation of the amine, which is then followed by the rate-determining bimolecular reaction via the mechanism

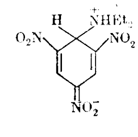
$$2\text{DEA} + \text{TNB} \rightleftharpoons (\text{DEA})_2 + \text{TNB} \rightleftharpoons Z \rightleftharpoons \text{TNB}.(\text{DEA})_2. \qquad (15)$$

(Z is an intermediate complex).

According to the results of a study[168] of the same reaction by the stopped flow method at room temperature, it proceeds in two consecutive stages, the first of which is rapid and reversible (TNB + DEA ⇌ K) and is of first order with respect to both components. The increase of the concentration of the complex K is found from the increase of absorption at 429 nm. The authors believe that the complex K differs from the charge-transfer complexes Z proposed by Caldin[167] and (LVII) in the mechanism (13) of Foster and Fyfe[55]. The first order with respect to DEA agrees either with the structure of the σ-complex (XL, Y = NEt$_2$) ($H_2\overset{+}{N}Et_2$ cation) or the zwitterionic complex (LX) formed via the direct interaction between *sym*-TNB and DEA.



(LIX)



(LX)

The second, slow stage involves further interaction of the complex K with associated acetone and DEA species, leading to the formation of a complex whose rate of accumulation was determined from its absorption at 516 nm. It is now clear from the work of Strauss[169,170] and Kohashi[98,99] that the final product isolated is the cyclic complex (LIX); similar complexes are formed particularly readily when secondary amines are used as alkaline agents[99,170]. It therefore becomes clear that in all the instances described, involving the use of diethylamine, the authors investigated different processes, predominating under the particular experimental conditions. Caldin[167] probably investigated the kinetics of the first, faster stage of the Janovsky reaction involving both the preliminary formation of the charge-transfer complex (LVII) [mechanism (13)] or Z [mechanism (15)] and the Janovsky complex (XXVIIIa). Although the interaction of *sym*-TNB with acetone in the presence of DEA is not considered in mechanism (15) proposed by the authors, evidently the final product, the rate of formation of which was measured, is in reality a Janovsky σ-complex of type (XXVIIIa). The observed considerable difference between the activation parameters and the orders with respect to DEA of the first rapid stage of the reaction in the studies of Caldin[167] and Osugi[168] is apparently caused by the different contributions of the charge-transfer complex and complex (XXVIIIa) to the measured rate of reaction. At higher temperatures Osugi and Sasaki[168] measured also the rate of the cyclisation reaction (which is not discussed in the present review), leading to the formation of bicyclic compounds of type (LIX) from compound (XXVIIIa) formed initially. The products of the further transformation of the Janovsky σ-complex (XXVIIIa) in an alkaline medium were investigated by Fyfe and Foster[55] [see mechanism (14)].

Features of another type were observed in a study of the kinetics of the interaction of *sym*-TNB and its derivatives with acetone[171] and cyclohexanone[172] in the presence of sodium methoxide. Thus the reaction of *sym*-TNB involves the initial formation of the methoxide σ-complex (XX) together with the Janovsky complex (XXVIIIa). The observed dependence of the initial rate of reaction on the concentration of *sym*-TNB shows that the stage involving attack by the acetonate ion via mechanism (16)–(18) is rate-limiting, and not the acetone deprotonation stage:

$$sym\text{-TNB} + CH_3O^- \xrightarrow{k_1} (\text{XX}),\ X = H,\ Y = NO_2\ , \qquad (16)$$

$$CH_3COCH_3 + CH_3O^- \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} \bar{C}H_2COCH_3 + CH_3OH\ , \qquad (17)$$

$$sym\text{-TNB} + \bar{C}H_2COCH_3 \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} (\text{XXVIIIa})\ . \qquad (18)$$

Comparison of the activation parameters of the Janovsky σ-complexes (XXVIIIa) and (XXXIX, X = NO$_2$)[171,172] with the known characteristics of the Meisenheimer σ-complexes (XX)[174,175] shows that the former are more stable.

According to Kimura et al.,[90] the type (XXI, R = X = OMe) σ-complex of 2,4,6-trinitroanisole and methoxide formed initially in an acetone–methanol medium is not solvolysed by acetone to (XXIV, X = OMe), as happens at high concentrations of the complex[83]; this requires an additional amount of methoxide. The change in the rate of generation of the colour as a function of the order in which sodium methoxide and 2,4,6-trinitroanisole are added is associated with the formation of diacetone alcohol from acetone via mechanisms (19) and (20); diacetone alcohol was detected chromatographically in a mixture of acetone and sodium methoxide. Thus the overall mechanism of the complex reactions occurring in the reaction system may be represented by Eqns. (17) and (19)–(21):

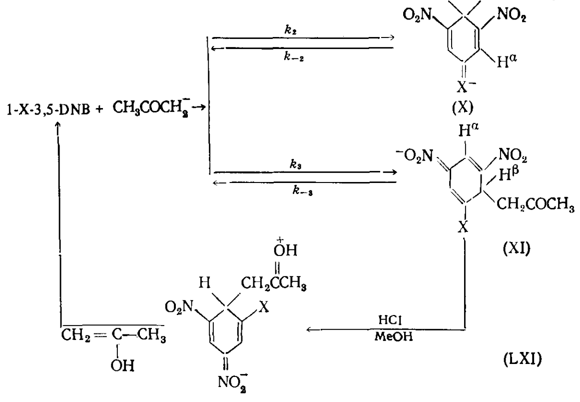
$$CH_3CO\bar{C}H_2 + CH_3COCH_3 \rightarrow CH_3COCH_2\text{–}C(CH_3)_2O^-\ , \qquad (19)$$

$$CH_3COCH_2C(CH_3)_2O^- + CH_3OH \rightarrow CH_3COCH_2C(CH_3)_2OH + CH_3O^-\ , \qquad (20)$$

$$2,4,6\text{-trinitroanisole} + \bar{C}H_2COCH_3 \rightarrow (\text{XXIV}),\ X = OMe,\ R = CH_2COCH_3\ . \qquad (21)$$

The kinetics of the interaction of *m*-DNB and its derivatives with acetone in an alkaline medium have been studied to an even lesser extent. Gitis and coworkers[175] showed that in aqueous acetone (15% H$_2$O) complexes of type (VII) are formed via a first-order reaction with respect to *m*-DNB and the alkaline agent. The reaction is faster when the alkaline agent and not *m*-DNB is added last to the solution, which is due to the consumption of alkali in side reactions with acetone. The authors believe that the results support mechanisms (9) and (10).

The kinetics of the formation of complexes by 1-X-3,5-dinitrobenzenes in a mixture with methanol and acetone[62] (X = COCH$_3$, CONMe$_2$, CONC$_5$H$_{10}$, or CONH$_2$) and cyclohexanone[111] (X = CN, COOMe, or CONC$_5$H$_{10}$) in the presence of sodium methoxide have been investigated. The authors believe that the reaction proceeds in two stages, the first of which [a reaction of type (17)] is much faster; this ensures a constant ratio of the concentrations of the MeO$^-$ ion and the ketone anion and the first order of the reaction with respect to these components. The rates of formation of both complexes are much higher than the rates of their decomposition and of the isomerisation of the symmetrical isomer (X) to the asymmetric isomer (XI). The latter is independent of the concentration of the methoxide, but increases with the methanol content, which indicates[62] isomerisation via the decomposition of (XI) to the initial nitro-compound:



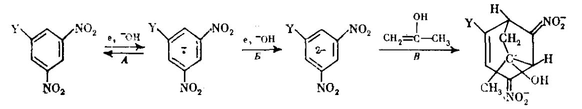
(22)

The quantities k_2 and k_3 increase with decrease of methanol concentration in solution and with increase of the electronegativity of the substituent X. The rate of formation of cyclohexanone complexes (XXXIX)[111] is 50 times greater than the rate of formation of acetone complexes[62]. According to the authors, this is due to the greater acidity of cyclohexanone (the concentration of its anion should be higher by three orders of magnitude). The weakening of nucleophilic properties and steric hindrance to a large extent diminish this effect. The authors[111] believe that acidification of the reaction mixture with HCl solution in methanol leads to the conversion of (XI) into the σ-complex (LXI) protonated at the carbonyl group, which then decomposes to the initial nitro-compound and the enolic form of acetone [reaction (22)].

Thus the kinetic data available at present do not permit unambiguous conclusions about the mechanism of the Janovsky reaction. As a rule, the conditions of the kinetic measurements (mixtures of acetone and other solvents, unusual alkaline agents such as DEA, MeO^-, etc.) are very markedly different from the conditions of the Janovsky reaction and the findings must be used with caution for the interpretation of its mechanism.

One should note that the majority of workers[62,90,167,168,171,175] treat the results of kinetic measurements within the framework of the traditional mechanisms (9)–(10) and (16)–(18). On the other hand, a number of facts have been discovered which do not fit within the framework of these ideas and require a detailed study of the elementary steps. This is, in the first place, the detection of the radical-anions of nitro-compounds in typical activated nucleophilic substitution reactions[176-182], so that a radical chain mechanism has been proposed for these processes[183-188]. The formation of oxygen in the Janovsky reaction, which has been detected polarographically both when an acetone solution of *m*-DNB is acted upon by KOH[189] and in the conversion of the "paired" complex (LII) into the σ-complex (XXVIII) in the presence of acetone and KOH[150], cannot be accounted for by mechanisms of types (9), (10), and (12). This suggests that the Janovsky reaction includes a stage involving electron transfer from the OH^- ion, the electron-donating properties of which are well known[190]. It appears that the evolution of oxygen is due to the decomposition in acetone of the hydrogen peroxide formed from the $\dot{O}H$ radicals after the electron transfer step. Quantitative formation of H_2O_2 in this process has been recently demonstrated experimentally[191,192]. Having observed the broadening of the proton signals of *sym*-TNB and the positive polarisation of the H^{β} protons of the σ-complex (XXVIII), Beletskaya and coworkers[86,87] do not rule out the possibility of the formation of intermediate radical species in the Janovsky reaction.

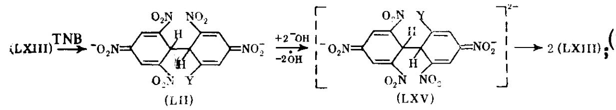
The role of electron transfer and the involvement of individual intermediate species in the elementary steps of the Janovsky reaction have been elucidated with the aid of electrochemical modelling. Polarographic reduction of *m*-DNB derivatives in DMF and acetone[189,193] showed that the reversible electron transfer at the potential of the first half-wave leads to the appearance of the radical-anions (LXII). It is seen from the results[194] of coulometric measurements in a circulation cell[195] that one electron is consumed in the reduction of *m*-DNB to (LXII, Y = H), while the addition of the second electron leads to the formation of the dianion (LXIII, Y = H), which interacts with acetone and gives rise to a doubly charged bicyclic complex with the postulated structure (LXIV, Y = H):



(23)

Coulometric measurements[194] have also shown that the formation of the corresponding intermediate complexes in the reaction of *sym*-TNB—the tentative bicyclic complex (LXIV, Y = NO_2) and the "paired" complex (LII)—also involves the consumption of two electrons; (LII) is then irreversibly reduced and gives rise to two (LXIII, Y = NO_2) species. The bicyclic complex (LXIV), formed on rapid interaction of the dianion (LXIII) with acetone, is fairly stable in an inert atmosphere. Under the influence of oxygen, (LXIV) is converted into the corresponding σ-complexes. Electrolysis at a controlled cathodic potential[194] made it possible to obtain the σ-complexes (VII) and (XXVIIIa), agreeing in terms of all characteristics with the complexes synthesised chemically[50,58].

The set of data obtained suggest[189,193,194] that the Janovsky reaction includes the same stages as the electrochemical reduction of aromatic polynitro-compounds in acetone with the sole difference that the electron donor in the former case is the hydroxide ion. In a general form the mechanism of this reaction may be supplemented, apart from Eqn. (23), by processes (24)–(26). The radical-anions (LXII) are generated in the first stage, some being converted under the influence of oxygen into the initial reactant and others being reduced by OH^- ions to the dianions (LXIII).



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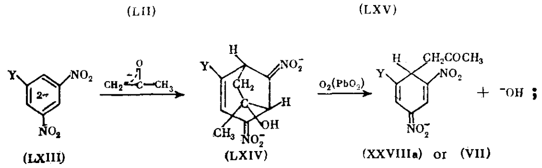


(25)

$$2\,{}^{-}OH \longrightarrow 2\,\dot{O}H \longrightarrow H_2O_2 \longrightarrow H_2O + {}^{1}\!/_{2}\,O_2 \ . \qquad (26)$$

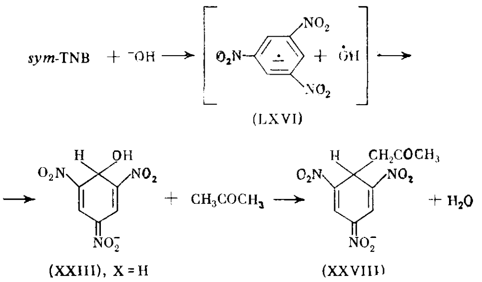
Owing to their high reactivity, they immediately undergo further transformations, attacking the double bond of the enolic form of acetone with formation of the bicyclic complexes (LXIV) via reaction (23). In the presence of an excess of a strong electron acceptor (*sym*-TNB) the interaction of the latter with the dianion (**LXIII**, Y = NO_2) leading to the paired complex (**LII**), is more likely. Under the influence of alkali, the latter is reduced (by the addition of two electrons) to (LXV), which dissociates into two dianions (**LXIII**) via mechanism (24). The compound (LXIV, Y = H or NO_2) formed subsequently is oxidised by oxygen and converted into the final product of the Janovsky reaction, namely the σ-complex (**VII**) or (XXVIIIa) respectively.

The majority of the intermediates indicated in mechanisms (23)–(25) have been identified in solutions in the course of electrochemical simulation or isolated in a free form. The structure of the bicyclic complexes (LXIV) was not demonstrated unambiguously[189,194], since, owing to their low stability, they cannot be isolated from the reaction solutions. The available experimental data show that they are doubly charged species; the absorption bands at 688 and 510 nm in the spectra of the reaction solutions have been assigned to (LXIV, Y = H) and (LXIV, Y = NO_2) respectively, the wavelengths being close to the maxima of the absorption bands of the bicyclic σ-complexes (LIX) obtained by Strauss[169,170] from *sym*-TNB. Mechanisms (23) and (25) explain the evolution of oxygen in the Janovsky reaction (26) and confirm the presence of the stage involving electron transfer from the OH^- ion in accordance with Eqn. (23) and subsequent dimerisation of $\dot{O}H$ radicals via mechanism (26).

When alkali is used as the electron donor in acetone solutions, it is not possible to detect the radical-anions of the initial nitro-compounds, because they are "quenched" by the oxygen evolved. This reaction stage was detected[196] by EPR when an acetone solution of *m*-DNB was treated with sodium thiophenoxide as the alkaline agent. Further reactions of the radical-anion formed from *m*-DNB lead, as in the Janovsky reaction with KOH, to the σ-complex (**VII**) as the final product. When potassium 2,4,6-tri-t-butylphenoxide, which has a low oxidation potential (−0.305 V relative to the saturated calomel electrode in DMF), is used as the electron donor in the reaction of acetone with *m*-DNB and *sym*-TNB in a 20 : 1 DMF–acetone mixture in an inert atmosphere, it is possible to detect by EPR the tri-t-butylphenoxy-radical, which is formed from the initial phenoxide as a result of electron transfer. Thus it proved possible in this experiment to detect directly for the first time species formed from the electron donor after the one-electron transfer step. As for the thiophenoxide, the final reaction products in this case are the σ-complexes (**VII**) and (**XXVIIIa**), which have been identified on the basis of their absorption spectra.

Data for the chemical simulation of this process constitute convincing confirmation of the involvement of the *m*-DNB dianion in the intermediate stage of the Janovsky reaction[197,198]. Using the method of homogeneous electron transfer from the dipotassium salt of the cyclo-octatetraene dianion (**LXIII**, Y = H) were obtained in quantitative yields. Experimental data showed that (LXII, Y = H) does not react Experimental data showed that (**LXII**, YH) does not react with acetone, a stable EPR signal, identical with that of the radical-anion formed by the electrochemical reduction of *m*-DNB[193] being observed under these conditions. On the other hand, when the *m*-DNB dianion (**LXIII**, Y = H) is treated with acetone, an unstable compound is formed and on contact with oxygen is rapidly converted into the Janovsky σ-complex (**VII**). The latter is formed as a result of the direct interaction of the dianion with acetone, since the σ-complex (**VII**) was not obtained on treating with acetone the *m*-DNB dianion subjected to a preliminary treatment with oxygen. Thus, of the two charged *m*-DNB species, only the dianion (**LXIII**, Y = H) interacts with acetone in the absence of alkali and forms the Janovsky complex (**VII**). Furthermore the product of the interaction of the *m*-DNB dianion with acetone has been converted into the σ-complex (**VII**) in the complete absence of oxygen but in the presence of another electron acceptor—lead dioxide[197]—which constitutes yet another demonstration of the presence of the stage involving the oxidation of the bicyclic product (LXIV) into the final σ-complex and of the overall reaction mechanism (23)–(26).

It has also been suggested[199] that the Janovsky reaction may proceed via the hydroxylated σ-complex (**XXIII**, X = H), the formation of which is preceded by electron transfer, the radical-anion of the polynitro-compound reacting with the $\dot{O}H$ radical in the cage (LXVI). Under the influence of a large excess of the ketone, this is followed by the displacement of the OH group by the acetone residue and the formation of the Janovsky σ-complex (**XXVIIIa**):



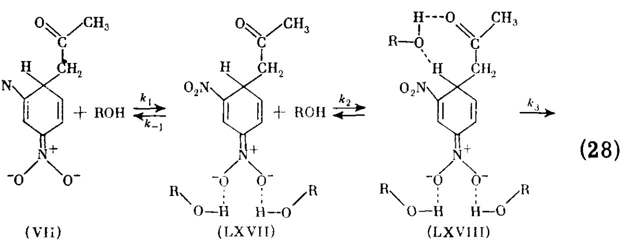
(27)

These conclusions are based on the fact that, when alkali is added to a solution of *sym*-DNB and an aromatic compound with activated methyl groups in DMSO, the σ-complex of *sym*-TNB with the OH^- anion of type (**XXIII**) is formed initially and then gradually converted into a complex of type (XL) with the above nucleophiles[153,154]. It has also been shown[91,136] that acetone and acetonitrile displace the OH group from σ-complexes of type (**XXIII**), forming more stable complexes of types (**XXVIII**) and (**VII**). A mechanism similar to mechanism (27) was then extended[175] to *m*-DNB in view of the observation that the reaction is of first order with respect to both alkali and *m*-DNB. However, it is noteworthy that the first order of the reaction with respect to KOH is also possible for mechanism (23) if stage (23*A*) or (23*B*) is rate-limiting. On the other hand, the identification of the radical-anions of the polynitro-compounds in the reaction solutions by EPR[176,183,196,200] shows that they emerge from the cage and can participate in other processes, differing from the pathway indicated by mechanism (27).

2. Decomposition of σ-Complexes by Proton-Donating Agents

The overall mechanism of the Janovsky reaction [Eqns. (9) and (10)] shows that the σ-complexes formed in an acid medium decompose to the initial nitro-compounds[48,50]. Whereas the decomposition of the *sym*-TNB complex (**XXVIIIa**) under these conditions requires a fairly concentrated acid, the *m*-DNB σ-complex (**VII**) undergoes slow decomposition[201–205] even in aprotic polar solvents (acetone, DMSO, DMF, etc.). The addition of other polar aprotic solvents (DMSO, DMF, etc.) to the acetone solution does not affect the rate of decomposition of the σ-complex (**VII**), while the introduction of an alcohol or water sharply increases it[201]. When the content of the proton-donating additive in the mixture is small (up to 4–6 M), the reaction is of first order with respect to both ROH and the complex undergoing decomposition, the second-order rate constants being proportional to the acidity of the alcohols employed.

The addition of large amounts of an alcohol (or water) to acetone leads to a deviation from the linear relation between lg*k* and N_{ROH}, which is due to the manifestation of the specific solvation of the complex by the alcohol or water. According to the authors[202], it occurs as a result of the formation of hydrogen bonds involving the nitro-groups, as in (LXVII), and the typical mechanism of the decomposition of σ-complexes of type (VII) by polar proton-donating solvents may be represented by the following scheme:



(VII) (LXVII) (LXVIII)

$$\longrightarrow m\text{-DNB} + \mathrm{ROH} + \mathrm{CH_3COCH_3}\ . \qquad (28)$$

One should note that the second nitro-group can also participate in the formation of hydrogen bonds with the solvent. The decomposition is then a second-order reaction, whose rate is determined by the rate of formation of the intermediate complex (LXVIII) ($k_3 \gg k_2$). Together with *m*-DNB, a certain amount of 2,4-dinitrophenylacetone was detected [Eqn. (30)].

At high concentrations of the proton-donating solvent the influence of structure formation in the solvent is superimposed on this process, apart from the solvation effect[202]. The decrease of the rate of decomposition of the σ-complex (VII) for a water mole fraction greater than 0.7 is associated with formation under these conditions of the three-dimensional structure of the framework characteristic of water, which greatly reduces the concentration of "free" H_2O molecules attacking the σ-complex in accordance with mechanism (28).

A change in the composition of the mixed solvent influences not only the rate of decomposition of the σ-complex (VII) but also its optical characteristics ($\lambda_{\max}$ and $\epsilon_{\max}$). It has been shown by ^{1}H NMR[202] that this does not entail the substitution of the acetone residue in (VII) by the conjugate base of the solvent with formation of complexes of the type (XX, X = Y = H).

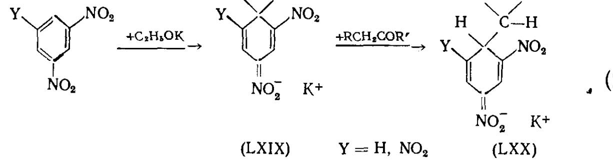
The stability of the σ-complexes of *m*-DNB derivatives increases as the electron-accepting properties of the substituent X are enhanced and the change in the first-rate constant is largely determined by the entropy factor[203,204]. A linear correlation is observed between the values of σ_X for the substituent and the logarithms of the decomposition rate constants[204] for isomers (IV) and (V); the sensitivity constant ρ for the latter isomer is twice as high as for the former. The authors believe that the cyclohexadiene system of the σ-complexes (IV) and (V) has a capacity for transmission of electronic effects close to that of an aromatic structure. Both in the decomposition by water in acetone[203,204] and in the reversible acid-catalysed decomposition in an acetone–methanol medium[62], the rate of decomposition of "symmetrical" isomers of types (V) and (X) is much higher than for the "asymmetric" isomers (IV) and (XI). The decrease of the concentration of methanol and the increase of the electronegativity of X under these conditions lead to an insignificant diminution of the constants k_{-2} and k_{-3} for the decomposition of isomers (X) and (XI) [mechanism (22)], which the authors[62] attribute to a decrease of the degree of solvation of the anion by methanol. On passing from the "acetone" complex (XI, X = $\mathrm{CONC_5H_{10}}$)[62] to the analogous cyclohexanone complex[109], the stability of the σ-complex increases appreciably; it is believed that this is due to an additional energetically preferred interaction of the piperidine and cyclohexane rings.

When alkali is added[205] to an aqueous acetone solution of the σ-complex (VII), its decomposition is accelerated sharply. The first order of the reaction with respect to the initial compound and alkali and the dependence of lg K_{act} on the concentration of the alkaline agent suggested that the main step in the alkaline decomposition is attack by the OH^- ion on the σ-complex (VII).

Thus in the presence of proton-donating solvents, and in an acid medium, Janovsky σ-complexes decompose mainly to the initial compounds owing to solvation by the proton-donating component. On the other hand, the mechanism of the alkaline decomposition of type (VII) complexes still remains unelucidated.

3. Oxidation of σ-Complexes

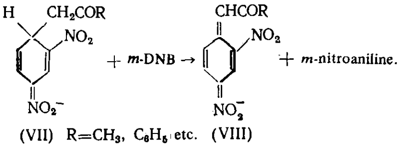
Detailed studies of the behaviour of type (VII) σ-complexes in the reaction system showed that, in the presence of an excess of the polynitro-compound, (VII) may be oxidised. This has been established in connection with the study of the mechanism of the Zimmermann reaction[206], which has been suggested for the analysis of ketosteroids with the aid of *m*-DNB (solvent—alcohol). Foreman et al.[110] initially proposed a reaction mechanism where the polynitro-compound reacts with the alkoxide in the first stage and gives rise to the complex (LXIX), while in the second stage the alcohol is displaced by the ketone with formation of a coloured salt, which has the general structure (LXX):



(LXIX) Y = H, NO₂ (LXX) (29)

However, it was found that in fact the type (LXX) σ-complex is oxidised by the excess of the nitro-compound under the reaction conditions.

The possibility of such oxidation was first suggested by Isidate and Skaguchi[207], who proposed the reaction mechanism



(VII) R=CH₃, C₆H₅ etc. (VIII) (30)

This course of the reaction in the presence of an excess of the nitro-compound was then demonstrated by numerous investigations[114,208-212]. Mechanism (30) has also been confirmed[209] by the similarity of the absorption spectra of the products of the interaction of acetone or acetophenone with *m*-DNB under the conditions of the Zimmermann reaction and the spectra of 2,4-dinitrophenylacetone or 2,4-dinitrobenzyl ketone in an alkaline medium, which had been noted earlier[38]. The results of spectrophotometric studies on the Janovsky and Zimmermann reactions are presented in a short review[210].

The agreement of the products of the Zimmermann reaction with structure (VIII) has been demonstrated convincingly by Kimura and coworkers[51,56], who isolated this compound in a free form, determined its structure, and demonstrated its difference from the Janovsky σ-complexes. The authors proposed a general mechanism (31) for the reaction of *m*-DNB in an alkaline medium, which is similar to mechanism (30):

$$m\text{-DNB} + \text{acetone} \xrightarrow{^{-}\text{OH}} (\text{VII}) \xrightarrow{\text{oxidation}} (\text{VIII}) \xrightarrow{^{-}\text{OH}} \text{unidentified products.} \qquad (31)$$

The polarographic reduction potentials of *m*-DNB (−0.62 V), the Janovsky complex (−0.68 V) and the Zimmermann complex (−0.63 V) which they measured[56] (at pH 13) hardly confirm the earlier view[206-209] that *m*-DNB can oxidise (VII) to (VIII). The authors[213] suggest that the oxidation stage is not rate-limiting in the Zimmermann reaction.

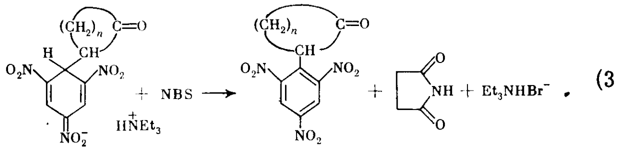
The study of the electrochemical mechanism of the oxidation[214] of Janovsky σ-complexes derived from *m*-DNB and *sym*-TNB showed that they are irreversibly oxidised in a single two-electron stage. Electrochemical oxidation and oxidation by manganese(III) acetate convert the σ-complex (VII) into 2,4-dinitrophenylacetone. The comparatively high oxidation potential of the σ-complex (VII) obtained ($E_{1/2} = +0.330$ V) shows that a fairly strong oxidant is necessary for the occurrence of the Zimmermann reaction.

Recent quantum-chemical calculations[151] showed that the benzenoid structure, in which the negative charge is distributed principally between the methylene carbon atom (−0.320) and the ring (−0.276), is largely retained in the anion (VIII) of 2,4-dinitrophenylacetone.

Thus it can be regarded as established that the Zimmermann reaction involving *m*-DNB and its derivatives consists in further oxidation of the Janovsky σ-complex by the excess of the nitro-compound with formation of more stable type (VIII) products. The insignificant amount of 2,4-dinitrophenylacetone formed in the decomposition of type (VII) σ-complexes by proton-donating agents [mechanisms (9) and (10)] is apparently due to oxidation by the excess of the *m*-DNB produced. On the other hand, the quantitative yield of the initial *sym*-TNB in the decomposition of its type (XXVIII) σ-complexes shows that reaction (30) does not occur here. This is evidently due to the greater stability of (XXVIIIa), whose oxidation requires a stronger oxidant, in conformity with its higher oxidation potential[214] ($E_{1/2} = +0.825$ V). Indeed, it has been shown for the oxidation of a number of σ-complexes (XL) by copper(II) oxide[159], chromium oxide[160], *p*-benzoquinone[164], tropylium tetrafluoroborate, and the bromine-pyridine adduct[165] that *sym*-TNB derivatives containing the corresponding aromatic or alicyclic groups in the 1-position are formed in high yields.

There are also other instances of the oxidation of σ-complexes by *sym*-TNB with retention of the added nucleophile. These include the conversion of the trianionic complex (XLVI) on oxidation with bromine into 2-methyl-4,6-dinitrocoumaran[142]. Wennerström and coworkers[162,164] oxidised a mixture of the isomers of (XL, Y = cyclopentadienyl) under mild conditions with *p*-benzoquinone or hydrogen peroxide in an acid medium to a mixture of 2,4,6-trinitrophenylcyclopentadienes and they also oxidised the σ-complex (XLm) or the corresponding nitronic acid (LVIb) to indenyl-2,4,6-trinitrobenzene.

The oxidation of the σ-complexes (LXXI), obtained in an earlier study[119], by *N*-bromosuccinamide in methanol at 0°C has been described[215]:



(LXXI) (LXXII) (32)

This led to the isolation of the ketones (LXXII) in a high yield. The reaction is of a general type and the complexes obtained from cyclopropyl methyl ketone and acetophenone are also readily oxidised to the corresponding trinitrophenyl ketones. The oxidation of asymmetric ketones, capable of giving rise to carbanions of different types, yields a mixture of products.

Many oxidants have been investigated by Kursanov and coworkers[216], who obtained 2,4,6-trinitrophenylacetone in 93% yield by oxidising the σ-complex (**XXVIIIa**) with tropylium tetrafluoroborate:

(33)

The authors showed that both two-electron (lead tetraacetate, hypohalogenites, and halogens) and one-electron (Fenton's reagent, silver nitrate, and ferric chloride) oxidants may be used, the rate and yield of the reaction depending on the standard potential of the oxidant. 1-Trihalogenomethyl-2,4,6-trinitrobenzenes have been obtained similarly from the σ-complexes (XL, Y = CCl_3, CBr_3, or CI_3) by oxidation with chlorine or bromine in t-butyl alcohol and pyridine.

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Schmidt Reaction with Aldehydes and Carboxylic Acids

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Modern views on the mechanism and applications are discussed. A list of 112 references is included.

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I. INTRODUCTION

In 1923 Schmidt, on investigating the reaction of hydrogen azide with various organic compounds, discovered that carbonyl compounds undergo rearrangement in the presence of acid catalysts[1]. Thus aldehydes are converted into formamides and nitriles, ketones into amides, and carboxylic acids into amines:

$$RCHO + HN_3 \xrightarrow{H+} RCN + RNHCHO \tag{1}$$

$$RCOR' + HN_3 \xrightarrow{H+} RCONHR' + RNHCOR' \tag{2}$$

$$RCOOH + HN_3 \xrightarrow{H+} RNH_2 \tag{3}$$

Some years later Braun and Österlin used this reaction to obtain aliphatic[2], alicylic[3], and aromatic[4] amines from carboxylic acids. Since that time the Schmidt reaction has found widespread application as a convenient method for obtaining *N*-substituted amides, amines, nitriles, and several other compounds.

Since the conversion of carboxylic acids into amines occurs with retention of optical activity[3,5], and is not accompanied by *cis-trans* isomerisation[6-8], it has been used as a convenient model in solving several important theoretical problems associated with the stereochemistry of molecular rearrangements[5,6]. The reaction of carboxylic acids with hydrogen azide has been employed to investigate the structure of alkaloids[9-11] and as an analytical method in studying the mechanism of the solvolysis of alkyl bromides[12].

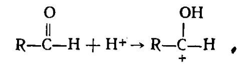
During recent years the Schmidt reaction has still been the subject of numerous investigations. Experimental results obtained up to 1962 were summarised by Wolff[13] and by Smith[14]. Surveys have recently appeared[15,16] on the Schmidt reaction with ketones. The present Review examines fresh results on the reactions of aldehydes and carboxylic acids with hydrogen azide, paying attention mainly to their mechanism and applications.

II. MECHANISM OF REACTIONS OF ALDEHYDES AND CARBOXYLIC ACIDS WITH HYDROGEN AZIDE

The action of hydrogen azide on aldehydes and carboxylic acids is an acid-catalysed reaction. Protic acids—sulphuric and polyphosphoric (in most cases the former)—are used as catalysts. In discussing the mechanism of these reactions we must obviously consider first of all the behaviour of the reactants in aqueous sulphuric acid.

1. Behaviour of Aldehydes, Carboxylic Acids, and Hydrogen Azide in Aqueous Sulphuric Acid

Aldehydes are weak organic bases and are protonated in aqueous sulphuric acid, with the proton adding to the carbonyl oxygen[17]:



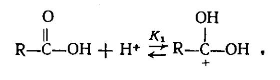
$$R{-}\overset{\overset{O}{\|}}{C}{-}H + H^+ \rightarrow R{-}\overset{\overset{OH}{|}}{\underset{+}{C}}{-}H \ , \tag{4}$$

A considerable number of studies have been made on the protonation of aldehydes, but in most cases aromatic aldehydes were investigated, since aliphatic aldehydes are unstable in aqueous mineral acids. The sole method for assessing the basicity of aliphatic aldehydes is therefore to measure the spectral shifts due to the hydrogen bond. On the basis of data at present available it may be postulated that pK_a values for the simplest aliphatic aldehydes lie between −7 and −8 H_0 units.

Protonation has been studied in greatest detail on substituted benzaldehydes. Basicity data were first obtained during the mid-1950s, when Schubert et al.[18], and later Yates and Stewart[19], made pK_a determinations on a large number of substituted benzaldehydes. It was postulated that these compounds were Hammett bases. Their basicity constants correlated well with the σ^+ constants of the substituents. The basicity of benzaldehyde of aqueous sulphuric acid has more recently been reinvestigated by several workers[20], who have concluded that protonation of this aldehyde is described better by the acidity function H_A than by H_0.

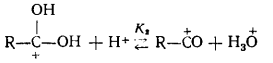
As previous determinations of the basicity constants of aldehydes had used out-of-date values for the acidity function of aqueous sulphuric acid, and in some cases employed insufficiently rigorous methods for processing the experimental results, a fresh study has recently been made[21,22] of the basicity of a series of substituted benzaldehydes. These compounds are protonated similarly to Hammett bases, except in the case of *p*-methoxybenzaldehyde, whose divergence is obviously due to specific solvation of the methoxy-group. Benzaldehyde and 1′-deuterobenzaldehyde in sulphuric and deuterosulphuric acids have almost identical basicities[23], and a similar situation is observed with the corresponding 2,4,6-trimethylbenzaldehydes[18]. The slight differences in the basicity constants are not due to variation in the acid–base properties of these compounds, since they lie within the limits of accuracy with which the ionisation ratios have been determined.

Like aldehydes, carboxylic acids are weak organic bases, and are protonated in aqueous sulphuric acid, with the proton adding to the carbonyl oxygen atom:



$$R{-}\overset{\overset{O}{\|}}{C}{-}OH + H^+ \overset{K_1}{\rightleftarrows} R{-}\overset{\overset{OH}{|}}{\underset{+}{C}}{-}OH \ . \tag{5}$$

The basicity of carboxylic acids has been investigated in some detail[17], for study of the mechanisms of acid-catalysed reactions involving carboxylic acids, including the Schmidt reaction, is impossible in the absence of knowledge of their equilibrium constants in mineral acids. Depending on the acidity of the medium, furthermore, protonated carboxylic acids may undergo secondary ionisation to form acylium ions[24,25]



$$R-\overset{\overset{\displaystyle OH}{|}}{\underset{+}{C}}-OH + H^+ \overset{K_2}{\rightleftarrows} R-\overset{+}{C}O + H_3\overset{+}{O} \qquad (6)$$

which provide a convenient model in studies of the properties and the structure of carbonium ions[26,27].

The basicity of aliphatic carboxylic acids has been investigated by ultraviolet, infrared, and nuclear magnetic resonance spectroscopy. Some workers assumed that these acids are Hammett bases[28,29]. During recent years, however, this view has been criticised, and it is suggested that such acids as acetic are protonated by a so called hydration mechanism[30,31].

The protonation of aromatic carboxylic acids has been widely investigated. The early work showed that substituted benzoic acids are Hammett bases[32,33]. Later results indicated[34–37] that the protonation of benzoic acids is not described by the acidity function H_0. Such deviations have been observed in the protonation of salicylic[37], 2,2′-diphenic[34], and *o*-benzoylbenzoic[35] acids. For the latter acids this might be due to secondary ionisation of the protonated compound and formation of an acylium ion. Vinnik et al. [38] pointed out the difficulties arising in the interpretation of experimental results on the protonation of such acids. Ultraviolet and n.m.r. spectroscopy have recently been used to study the basicity of a series of mono-, di-, and tri-substituted benzoic acids in aqueous sulphuric acid[39]. It was concluded that, despite some inconsistency in available data, there are grounds for supposing that substituted benzoic acids are protonated similarly to Hammett bases. With benzoic acid a temperature dependence of protonation and the basicity have been studied in deuterosulphuric acid[39].

With increase in the concentration of sulphuric acid, as already noted, protonated carboxylic acids may undergo dehydration with formation of acylium ions. Investigation by n.m.r. spectroscopy of the behaviour of a series of aliphatic carboxylic acids in concentrated sulphuric acid or oleum showed[26] that e.g. with acetic acid reaction (6) is observed in 15% oleum, but a still more acid medium is required for propionic and isobutyric acids. Data on the formation of aromatic acylium ions, obtained in a study of the cryoscopic properties of solutions of benzoic acids in concentrated sulphuric acid[24,40], showed that formation of acylium ions is favoured by the presence of two electron-donor *ortho*-substituents in the benzene ring. This is obviously because such substituents stabilise the acylium ion and destabilise the protonated form of benzoic acid. For 2,4,6-trimethylbenzoic acid attempts were made[25,41] to estimate the equilibrium (6) constant, by means of the acidity functions H_0 and I_0 respectively. It was shown subsequently, however, that such processes should be described by the acidity function H_R.[42,43] Indeed, in the case of 2,4,6-trimethylbenzoic acid formation of the acylium ion is well described[39] by this last acidity function, with $pK_a = -19.87$.

It must be emphasised that published data obtained by different workers on the basicity of particular carbonyl compounds are often difficult to compare, for inadequate methods of calculating ionisation ratios are used in processing the experimental results. Yet it has been noted repeatedly[33,44] that this stage is extremely important in studying the basicity of organic bases. Certain difficulties arise also in discussing the basicity constants of aldehydes and carboxylic acids obtained by different physicochemical methods, especially nuclear magnetic resonance. The reasons have been examined by several workers[17,39,45]. Finally, it is obviously a simplification to describe the protonation of aldehydes and carboxylic acids by means of the Brønsted equations (4) and (5).

It has recently been suggested that carbonyl compounds are protonated by a "dehydration" mechanism[46]:

$$\begin{gathered} B\cdot b\ H_2O + H^+\cdot x\,H_2O \rightleftarrows B\ \cdots\ H^+\cdot n\,H_2O + (b+x-n)\,H_2O \\ B\ \cdots\ H^+\cdot nH_2O \rightleftarrows B\ \cdots\ H^+\cdot(n-1)\,H_2O + H_2O \\ \cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots \\ B\ \cdots\ H^+\cdot H_2O \rightleftarrows \overset{+}{B}H + H_2O \end{gathered} \qquad (7)$$

where B is the base (aldehyde or carboxylic acid). The occurrence of such processes in the protonation of weak organic bases has been established quite convincingly by laser Raman spectroscopy[47,48]. This view is supported also by kinetic data on certain acid-catalysed reactions[46], including the Schmidt reaction[49]. However, the lack of constants of the equilibria (7) presents certain difficulties in interpreting the kinetic results.

Table 1. Basicity of hydrogen azide determined by various methods.

Method	$-pK_a(H_2N_3^+)$	Ref.
Partition in $CHCl_3$–H_2SO_4	6.9	51
Vapour pressure (Henry's law)	7.02	52
Ultraviolet spectroscopy	7.19	55
Kinetic data	5.4	53
	6.6	54

Hydrogen azide is protonated in aqueous sulphuric acid

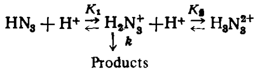
$$HN_3 + H^+ \rightleftarrows H_2\overset{+}{N}_3 \qquad (8)$$

$$H_2\overset{+}{N}_3 + H^+ \rightleftarrows H_3N_3^{2+} \qquad (9)$$

a possibility first pointed out by Hantzsch[50]. More recently Bak and Praestgaard[51] found by a partition method that the basicity of hydrogen azide is $pK_a(H_2N_3^+) = -6.9$. Almost the same value has been obtained (−7.02) by measuring the vapour pressure over solutions of perchloric acid[52], and kinetic methods yield similar results[53,54]. It has been postulated in all cases that hydrogen azide is a Hammett base. Study of its basicity by ultraviolet spectroscopy has shown[55] that its protonation is actually described by the acidity function H_0. Table 1 gives values obtained by different methods for the basicity of hydrogen azide. The approximate value obtained by Hantzsch[50] for singly protonated hydrogen azide was $pK_a(H_3N_3^{2+}) \approx -10.2$. Recent kinetic determinations[54,55] give limits of −9.60 and −9.99 H_0 units. The basicity of deuterium azide in a D_2O–D_2SO_4 mixture obtained by ultraviolet spectroscopy[56] differs from the value for hydrogen azide: $pK_a(D_2N_3^+) = -7.56$.

In studying the mechanism of the Schmidt reaction it must be borne in mind that hydrogen azide decomposes in aqueous mineral acids[57]. In 73.8–98.7% sulphuric acid at

60°C the decomposition is an acid-catalysed process[55], the activated species being $H_2N_3^+$. The mechanism of this reaction can be represented as



$$HN_3 + H^+ \overset{K_1}{\rightleftarrows} \underset{\underset{\text{Products}}{\downarrow k}}{H_2N_3^+} + H^+ \overset{K_2}{\rightleftarrows} H_3N_3^{2+} \qquad (10)$$

where K_1 and K_2 are the basicity constants of HN_3 and $H_2N_3^+$ respectively, and k is the true rate constant. The effective rate constant is then related to the true rate constant by the formula

$$k_{\text{eff}} = \frac{k}{K_1/h_0 + h_+/K_2 + 1},$$

or

$$k_{\text{eff}} = k \cdot A, \qquad (11)$$

in which

$$A = (K_1/h_0 + h_+/K_2 + 1)^{-1}.$$

The equation to the regression line for the dependence (11) is

$$\lg k_{\text{eff}} = (0.85 \pm 0.05) \lg A - (2.18 \pm 0.02)$$
$$r = 0.98; \; n = 14; \; s = 0.05 \; . \qquad (12)$$

Kinetic results obtained in 73.8–89.6% sulphuric acid, in which the activity of water is quite high, were treated by Bunnett's method[58] in conformity with the equation

$$\lg k_{\text{eff}} - \lg \frac{h_0}{h_0 + K_1} = \omega \lg a_{H_2O} + c. \qquad (13)$$

The equation to the regression line is

$$\lg k_{\text{eff}} - \lg \frac{h_0}{h_0 + K_1} = (0.13 \pm 0.03) \lg a_{H_2O} + (1.80 \pm 0.06)$$
$$r = 0.91; \; n = 7; \; s = 0.02.$$

The value of $\omega < 1$ indicates that water is not involved in forming the activated complex.

Table 2. Activation energy of decomposition of hydrogen azide.

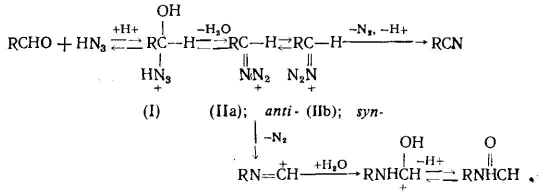
H_2SO_4, %	75.9	86.3	96.3
E_a, kcal mole^{-1}	31.2	23.2	19.8

Additional information on the mechanism of the decomposition of hydrogen azide has been obtained from a study of the kinetics at different temperatures. Table 2 shows that the activation energy does not remain constant with variation in the concentration of sulphuric acid. This is obviously due to partial change in the reaction mechanism on passing from the dilute to the concentrated acid. It may be postulated that non-protonated hydrogen azide also decomposes, although the rate is considerably smaller than that of the main reaction. Some departure from unity in the slope of the relation (12) is obviously due to the same causes. Kinetic study shows[56] that the decomposition of deuterium azide in $D_2O + D_2SO_4$ has the same mechanism as that of hydrogen azide ($k_D/k_H \simeq 4$).

The acid–base equilibria preceding the reaction of aldehydes and carboxylic acids with hydrogen azide must be borne in mind when studying its mechanism. The basicity constants of carbonyl compounds and hydrogen azide required for calculation of the reaction rate constants should be determined under comparable conditions.

2. Mechanism of Reaction of Aldehydes with Hydrogen Azide

It was assumed earlier that the Schmidt reaction had the same mechanism for aldehydes and for ketones. Thus McEwen et al.[59] and later Smith and Antoniades[60] supposed that, by analogy with ketones, aldehydes react in the protonated form with hydrogen azide; the resulting protonated azidoalkanol (I) loses water to give the iminodiazonium ion (II), which is subsequently converted into the reaction products:



(14)

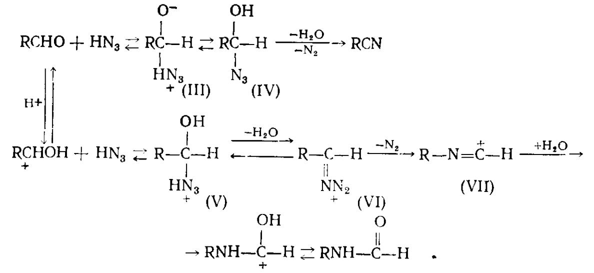
It is generally accepted for unsymmetrical ketones[15] that the iminodiazonium ion can exist as *syn* and *anti* isomers. The more bulky substituent, located in the *anti* position with respect to the diazo-group, migrates to the nitrogen atom to form an iminocarbonium ion. This important postulate will explain the preferential formation of one of the isomeric amides in the Schmidt reaction with ketones. Hence the corresponding formamide should be the sole reaction product in the case of aldehydes. In fact, however, nitriles are formed together with formamides when aldehydes react with hydrogen azide[61]. In order to explain this inconsistency it was suggested[59] that formation of the nitrile form the *syn*-iminodiazonium ion (IIb) involves detachment of a proton by the action of such a base as water or the hydrogen sulphate ion.

Subsequent detailed kinetic study of the reaction of aldehydes with hydrogen azide established that this postulate was incorrect. Furthermore, fresh results were obtained showing that the Schmidt reaction had different mechanisms with ketones and with aldehydes: ketones react in the protonated form, whereas aldehydes react in both protonated and non-protonated forms[62]. This explains the formation of two products — a nitrile and a formamide — in proportions depending on the acidity of the medium[63]: the proportion of formamide in the product increases with acidity, and the nitrile is favoured by diminished acidity. For example, the only product of the reaction of benzaldehyde with hydrogen azide in 71.2% sulphuric acid, in which the protonated form of the aldehyde is almost completely absent, is benzonitrile, but in the 87.4% acid only formanilide is produced. The ratio of the reaction products changes precisely in the range of sulphuric acid concentrations in which the acid–base equilibrium of benzaldehyde is observed. This enables the ratio to be calculated by means of the equation

$$\lg F = \mathrm{p}K_a - H_0, \qquad (15)$$

where $F = [\text{Fo}]/[\text{H}]$ is the ratio of the final concentrations of formamide and nitrile, $\mathrm{p}K_a$ relates to the conjugate acid of the aldehyde, and H_0 is the Hammett acidity function. Hence the formation of nitriles and formamides form aldehydes and hydrogen azide can be regarded as two parallel reactions involving respectively non-protonated and protonated forms of the aldehyde.

Thus the mechanism of the reaction of aldehydes with hydrogen azide can be represented



$$\mathrm{RCHO + HN_3 \rightleftarrows R\overset{O^-}{\underset{\overset{+}{H}N_3}{C}}{-}H \rightleftarrows R\overset{OH}{\underset{N_3}{C}}{-}H \xrightarrow[-N_2]{-H_2O} RCN}$$

$$\mathrm{R\underset{+}{C}HOH + HN_3 \rightleftarrows R{-}\overset{OH}{\underset{\overset{+}{H}N_3}{C}}{-}H \underset{}{\overset{-H_2O}{\rightleftarrows}} R{-}\underset{\overset{+}{N}N_2}{\overset{}{C}}{-}H \xrightarrow{-N_2} R{-}N{=}\overset{+}{C}{-}H \xrightarrow{+H_2O} RNH{-}\overset{OH}{\underset{+}{C}}{-}H \rightleftarrows RNH{-}\overset{O}{\overset{\|}{C}}{-}H} \quad (16)$$

Interaction of the non-protonated aldehyde with the azide forms the ambipolar ion (III), which isomerises into the azidoalkanol (IV). The latter is converted into the nitrile by dehydration and the elimination of nitrogen.

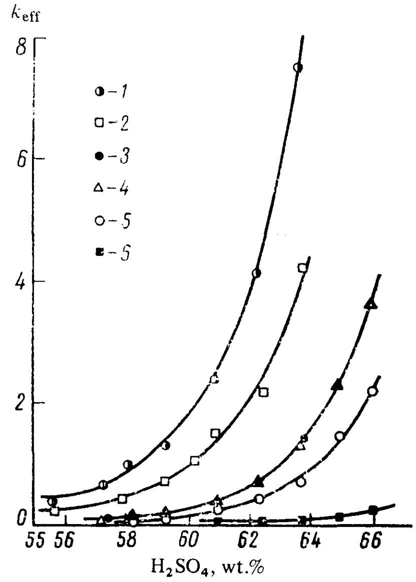


Figure 1. Influence of concentration of sulphuric acid on effective rate constants of the reaction of hydrogen azide with benzaldehydes containing various substituents:
1) *p*-methyl; *2*) none; *3*) *p*-chloro; *4*) *p*-bromo;
5) *m*-chloro; *6*) *m*-nitro.

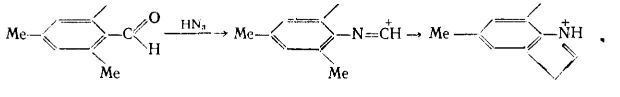
Such a reaction mechanism is quite consistent with the kinetic results. Kinetic study of the action of a series of substituted benzaldehydes[49] on hydrogen azide is moderately concentrated aqueous sulphuric acid, in which the non-protonated form of the aldehyde is reactive, has established a monotonic increase in reaction velocity with acid concentration (Fig. 1). This is because the aldehyde reacts as a complex with a hydrated proton. When weak organic bases (aldehydes) dissolve in aqueous mineral acids, such complexes $B\ldots H^+.nH_2O$ are supposed[46] to be formed (scheme 7). As the mineral acid becomes more concentrated, these complexes undergo dehydration to the protonated base. This involves a gradual advance by the proton from the "initial position of attack" [46] to the aldehydic oxygen atom, which tends to increase the reactivity of the complex. It thus becomes clear why the rate of reaction of the non-protonated aldehyde with hydrogen azide increases with the sulphuric acid concentration.

True rate constants for each type of complex cannot be calculated because of the absence of values for the equilibrium (7) constants. This leads to some difficulties in determining the limiting stage, since the ρ–σ method cannot be used for these purposes. However, existing data suggest that addition of hydrogen azide to the non-protonated aldehyde is the rate-determining stage. This is supported by a study[23] of the kinetic isotope effect in the reaction of benzaldehyde with hydrogen azide and by activation parameters (Table 3) †, which are typical of nucleophilic addition at a carbonyl group. The opposite kinetic isotope effect is observed for the reaction of benzaldehyde with hydrogen azide in D_2SO_4 in comparison with H_2SO_4: $k_D/k_H \simeq 4$. Yet no kinetic isotope effect is observed when benzaldehyde is replaced by 1′-deuterobenzaldehyde in sulphuric acid[23].

Table 3. Activation parameters for reaction of benzaldehyde with hydrogen azide.

$[H_2SO_4]$, %	E_a, kcal mole^{-1}	$H^{\neq}$, kcal mole^{-1}	$\Delta S^{\neq}$, e.u.
53.1	14.6	14.0	−12.8
55.6	15.6	14.9	−9.1
57.9	15.3	14.7	−8.1

According to Eqn. (16) the first stage in concentrated aqueous sulphuric acid is addition of hydrogen azide to the protonated aldehyde to form the protonated 1-azido-alkanol (V). Dehydration of (V) gives the iminodiazonium ion (VI), which eliminates nitrogen and undergoes rearrangement to the iminocarbonium ion (VII). The action of water on this ion (VII) yields the formamide. Existence of an iminocarbonium ion as an intermediate species is confirmed by the formation of "anomalous products" with certain aldehydes. Thus the reaction between 2,4,6-trimethylbenzaldehyde and hydrogen azide yields not only 2,4,6-trimethylformanilide but also the cation of 5,7-dimethylindole[22] as a result of intramolecular attack by the iminocarbonium ion on the carbon of an adjacent methyl group:



(17)

The kinetics of the reaction of aldehydes with hydrogen azide in concentrated aqueous sulphuric acid has been studied in detail. For a series of substituted benzaldehydes[62,64] the steady-state principle is applicable to the reaction, since intermediate products accumulate neither before nor

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† The slight increase in entropy of activation is fully consistent with the postulate that aldehydes react as complexes having different degrees of hydration.

after the rate-determining stage. The relation between the true rate constant k' and the effective constant k_{eff} is then

$$k_{\mathrm{eff}} = \frac{k' \cdot h_0}{(K_1 + h_0)\,(1 + h_0/K_2 + h_0 \cdot h_+/K_2 \cdot K_3)} \tag{18}$$

or

$$\lg k_{\mathrm{eff}} = \lg A + \lg k', \tag{19}$$

where

$$A = h_0/[(K_1 + h_0) \cdot (1 + h_0/K_2 + h_0 \cdot h_+/K_2 \cdot K_3)],$$

h_0 and h_+ are the Hammett acidity of the medium and the acidity for singly charged cations, K_1 is the basicity constant of the aldehyde, and K_2 and K_3 are those of hydrogen azide and of its monoprotonated form. Thus for benzaldehyde in 90.5–97.8% sulphuric acid good correlation is observed between $\lg k_{\mathrm{eff}}$ and $\lg A$ (formula 19). The equation to the regression line is

$$\lg k_{\mathrm{eff}} = (0.99 \pm 0.05) \lg A + (5.05 \pm 0.09)$$

$$r = 0.99;\ n = 8;\ s = 0.05.$$

The action of hydrogen azide on aldehydes is a multistage process, so that the true rate constant k' calculated by means of Eqn. (18) can be assigned to any of these stages—addition of hydrogen azide to the aldehyde, dehydration, or rearrangement.

Table 4. Rate constants of reactions of substituted benzaldehydes RC_6H_4CHO with hydrogen azide in H_2SO_4 (at 20° C).

R	$[H_2SO_4]$, %	$10^{-3}k_{\mathrm{eff}}$, $M^{-1}\ \mathrm{min}^{-1}$	$\lg k'$	R	$[H_2SO_4]$, %	$10^{-3}k_{\mathrm{eff}}$, $M^{-1}\ \mathrm{min}^{-1}$	$\lg k'$
p-CH_3	89.0	0.101	—	p-Br	94.5	0.176	5.63
p-CH_3	90.2	0.044	4.10	p-Br	97.6	0.032	
p-CH_3	92.8	0.019	—				
H	96.3	0.021	5.05	m-Cl	96.7	0.407	6.60
H	97.8	0.008		m-Cl	98.3	0.121	
p-Cl	90.0	0.601		m-NO_2	95.8	3.640	
p-Cl	92.7	0.458	5.52	m-NO_2	97.6	2.890	7.63
p-Cl	95.8	0.086					

The method of ρ–σ analysis has been successfully applied to ascertain the rate-determining stage[64]. Thus the true rate constants of substituted benzaldehydes (Table 4) correlate with the substituent constants σ^+. The equation to the regression line is

$$\lg k' = (3.515 \pm 0.091)\,\sigma^+ + (5.126 \pm 0.032),$$

$$r = 0.99;\ n = 6;\ s = 0.02.$$

From the absolute magnitude and the sign of the reaction constant ρ the limiting stage in the reaction of benzaldehydes, as with ketones[65], is addition of non-protonated hydrogen azide to the protonated aldehyde.

3. Mechanism of Reaction of Carboxylic Acids with Hydrogen Azide

The mechanism of the reaction of carboxylic acids with hydrogen azide was not discussed at all in the early work. The first attempt is evidently that by Briggs and Lyttleton[66], who tried to formulate a mechanism on the basis of a study of a series of substituted benzoic acids. A little later Newman and Gildenhorn[67] suggested a mechanism for the acid-catalysed reaction. They considered that the carboxylic acid reacts either in a protonated form or as an acylium ion; in either case the final products are the corresponding amine and carbon dioxide.

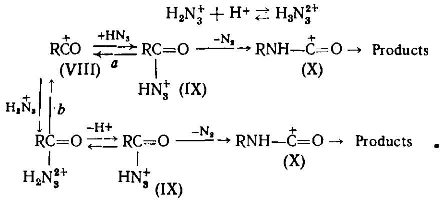
In a subsequent study of the Schmidt reaction with various carboxylic acids and also a detailed kinetic study fresh data were obtained largely supplementing and refining these views. Taking into account the protolytic equilibria preceding the main process, we can represent the mechanism of the reaction with carboxylic acids as

$$RCOOH + H^+ \rightleftarrows [RCO_2H_2]^+ \tag{20}$$

$$[RCO_2H_2]^+ + H^+ \rightleftarrows R\overset{+}{C}O + H_3O^+ \tag{21}$$

$$HN_3 + H^+ \rightleftarrows H_2N_3^+ \tag{22}$$

$$H_2N_3^+ + H^+ \rightleftarrows H_3N_3^{2+} \tag{23}$$



(24)

Such a mechanism is fully consistent with kinetic studies[57,68–70].

Table 5. Kinetics of reaction of 2,4,6-trimethylbenzoic acid with hydrogen azide in H_2SO_4 (at 15° C).

Expt.	$[H_2SO_4]$, %	$-H_0$	$\lg k_{\mathrm{eff}}$	Expt.	$[H_2SO_4]$, %	$-H_0$	$\lg k_{\mathrm{eff}}$
1	77.2	6.84	0.41	11	92.2	9.28	2.12
2	79.0	7.12	0.85	12	93.5	9.50	2.23
3	80.9	7.44	1.25	13	95.1	9.80	2.26
4	83.8	7.87	1.74	14	96.5	10.08	2.28
5	86.1	8.25	1.94	15	97.3	10.24	2.22
6	87.5	8.48	2.06	16	98.7	10.46	2.13
7	88.9	8.72	2.09	17	99.3	10.76	1.90
8	89.6	8.84	2.12	18	99.8	11.18	1.44
9	90.5	9.00	2.09	19	100.0	11.84	0.28
10	91.0	9.10	2.08				

Important results have been obtained for the reaction of 2,4,6-trimethylbenzoic acid with hydrogen azide in 77.2 to 100% sulphuric acid (Table 5 and Fig. 2).[70] The dependence of the logarithm of the effective reaction rate constant on the acidity function of the medium H_0 exhibits a characteristic break in the range 88.9–95.1% sulphuric acid (Fig. 2). The reaction velocity successively increases, decreases, and again increases in this acidity range, in which the content of the acylium ion increases sharply[39], while the proportion of free hydrogen azide decreases[55]. The explanation for such a complicated dependence of $\lg k_{\mathrm{eff}}$ on H_0 is that both free and protonated forms of hydrogen azide react with the acylium ion of 2,4,6-trimethylbenzoic acid.

The kinetic equation describing this process is

$$k_{\text{eff}}\frac{K_2}{h_R}\left(1+\frac{K_1}{h_0}+\frac{h_R}{K_2}\right)\left(1+\frac{K_3}{h_0}+\frac{h_+}{K_4}\right)=K'k'\frac{K_3}{h_0}+K''k'' \qquad (25)$$

or

$$k_{\text{eff}}D=K'k'\,\frac{K_3}{h_0}+K''k'', \qquad (26)$$

where K_1, K_3, and K_4 are the basicity constants of the carboxylic acid, hydrogen azide, and monoprotonated hydrogen azide, K_2 is the equilibrium constant for protonated acid and acylium ion, k' and k'' are the true rate constants of reactions (*a*) and (*b*) respectively (scheme 24), K' and K'' are the equilibrium constants of the stages preceding the rate-determining stage, h_0, h_R, and h_+ are the Hammet acidity of the medium and the acidities for triarylmethanols and singly charged cations, and

$$D=\frac{K_2}{h_R}\left(1+\frac{K_1}{h_0}+\frac{h_R}{K_2}\right)\left(1+\frac{K_3}{h_0}+\frac{h_+}{K_4}\right).$$

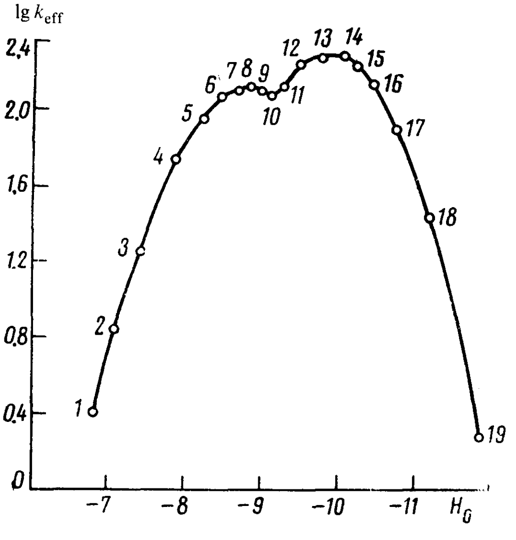


Figure 2. Dependence of effective rate constant for reaction of 2,4,6-trimethylbenzoic acid with hydrogen azide on the acidity function (for numbering of points see Table 5).

Under the boundary conditions with $h_0 \ll K_4$ or $h_0 \gg K_3$ (path *a* or *b*) Eqn. (25) becomes

$$\lg k_{\text{eff}}=\lg K'k'+\lg B \qquad (27)$$

$$\lg k_{\text{eff}}=\lg K''k''+\lg C, \qquad (28)$$

where

$$B=\frac{K_3h_R}{K_2h_0\,(1+K_1/h_0+h_R/K_2)\,(1+K_3/h_0+h_+/K_4)}$$

$$C=\frac{h_R}{K_2\,(1+K_1/h_0+h_R/K_2)\,(1+K_3/h_0+h_+/K_4)}\,.$$

Statistical treatment of the experimental results gave equations to the regression line for relations (27), (26), and (28) — experiments 1–6, 7–13, and 14–19 respectively (Table 5):

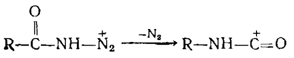
$$\lg k_{\text{eff}}=(4.26\pm 0.08)+(0.51\pm 0.17)\lg B, \qquad (29)$$
$$r=0.99;\ n=6;\ \alpha=0.975;\ f=12;$$

$$\lg k_{\text{eff}}\,D=(1.23\pm 0.35)\cdot 10^6\frac{K_3}{h_0}+(5.66\pm 35)\cdot 10^2; \qquad (30)$$
$$r=0.99;\ n=7;\ s=3.4\cdot 10^3;$$

$$\lg k_{\text{eff}}=(3.98\pm 0.06)+(1.39\pm 0.04)\lg C; \qquad (31)$$
$$r=0.97;\ n=6;\ \alpha=0.95;\ f=12.$$

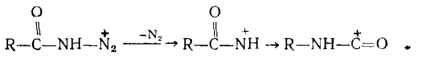
Good correlation of $\lg k_{\text{eff}}$ with $\lg B$ and with $\lg C$ is observed (Eqns. 29 and 31), which confirms the mechanism of the reaction of carboxylic acids with hydrogen azide (scheme 24). However, the slopes of these relations differ from unity. For this reason Eqns. (29)–(31) cannot be used to calculate the true rate constants k' and k''. Thus the reactive species is the acylium ion (VIII). In moderately concentrated sulphuric acid the first stage involves addition of free hydrogen azide to this ion (path *a*). At high acidities the protonated form reacts with the acylium ion (path *b*). In media of intermediate acidity the reaction occurs by a mixed mechanism. Independently of the reaction path (*a*) or (*b*) the first stage involves formation of the protonated acyl azide (IX). Elimination of nitrogen and rearrangement convert (IX) into the protonated isocyanate (X), which then reacts with water to give the reaction products.

Unfortunately, existing data do not permit an assessment of the mode of rearrangement of the acyl azide (IX) — whether in one stage



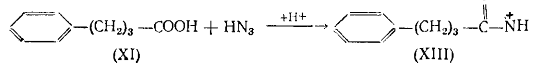
$$R{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}NH{-}\overset{+}{N}_2 \xrightarrow{-N_2} R{-}NH{-}\overset{+}{C}{=}O \qquad (32)$$

or in two stages



$$R{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}NH{-}\overset{+}{N}_2 \xrightarrow{-N_2} R{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}\overset{+}{N}H \rightarrow R{-}NH{-}\overset{+}{C}{=}O\ . \qquad (33)$$

For example, the action of hydrogen azide on γ-phenylbutyric acid (XI) in the presence of sulphuric acid forms not only the corresponding amine but also the lactam (XII) [71], presumably by intramolecular attack by the positively charged nitrogen on an *ortho* carbon atom of the benzene ring in the intermediate ion (XIII):



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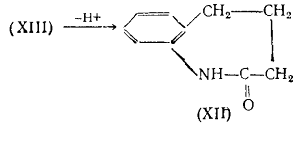
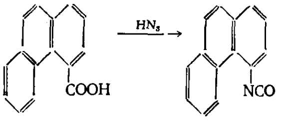


(35)

This suggests that rearrangement of the azide (IX) takes place in two stages. On the other hand, the lactam (XII) could be formed by a concerted mechanism with simultaneous detachment of nitrogen and electrophilic attack on the *ortho* carbon atom. Since there is no direct evidence in support of either mechanism, it is difficult to decide by which route (32 or 33) rearrangement of the protonated acyl azide takes place. Nevertheless, preference must be given to the synchronous mechanism by analogy with the Curtius reaction of the same type[72]. This suggestion is supported by the retention of configuration in the reaction of carboxylic acids with hydrogen azide[5–8, 73, 74].

Intermediate formation of an isocyanate from a carboxylic acid and hydrogen azide was demonstrated by Rutherford and Newman[75], who isolated the corresponding isocyanate in the reaction of phenanthrene-4-carboxylic acid:



(36)

The reaction of a carboxylic acid with hydrogen azide involves several stages, and the problem of which is rate-determining is important for an understanding of the overall mechanism. Kinetic results obtained[76] for a series of substituted benzoic acids in 99.9% sulphuric acid (Table 6) have been used to define the limiting stage. At this acid concentration ($H_0 = -11$) almost all the azide is present in the protonated form[55], and the reaction follows path (*b*) of scheme (24). The kinetics can then be represented by the equations

$$A^+ + B^+ \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} C^{2+} \underset{k_{-2}}{\overset{k_2}{\rightleftarrows}} C^+ \xrightarrow{k_3} D^+, \qquad (37)$$

$$[c] \qquad [d] \qquad [e]$$

where A^+ is the acylium ion, B^+ is the protonated hydrogen azide, C^{2+} and C^+ are the doubly and singly protonated acyl azide respectively, and D^+ is the protonated isocyanate. The effective rate constant k_{eff} is then related to the true rate constant k'' by Eqn. (28). Since no data are available on the acidity function H_R for sulphuric acid at concentration exceeding 99.9%,[39,43] equilibrium constants K_2 cannot be evaluated for substituted benzoic acids (except in the case of 2,4,6-trimethylbenzoic acid[39]). Hence formula (28) cannot be used to calculate the true rate constants for these compounds. This leads to difficulties when the Hammett equation is used to investigate the reaction mechanism. Nevertheless, under certain conditions effective rate constants can be used to correlate kinetic data for the action of hydrogen azide on substituted benzoic acids.

Table 6. Second-order rate constants for reaction of substituted benzoic acids RC_6H_4COOH with hydrogen azide in 99.9% H_2SO_4 (at 60° C).

Cpd.	R	k_{eff}, $M^{-1}\,min^{-1}$	Cpd.	R	k_{eff}, $M^{-1}\,min^{-1}$
1	H	12.59	5	*m*-F	2.34
2	*p*-Cl	8.32	6	*m*-NO_2	0.32
3	*p*-Br	8.32	7	*p*-NO_2	0.24
4	*m*-Br	3.31			

For scheme (37) either (*c*) or (*e*) can theoretically be the rate-determining stage, and they are indistinguishable kinetically. Only the protolytic equilibrium (*d*) is definitely not the limiting stage. If the rate constants k_1, k_{-1}, and k_3 are mutually comparable, the Hammett equation is quite inapplicable[77]. Provided that $k_1 \gg k_3$ or $k_3 \gg k_{-1}$, a correlation should be observed between $\lg k_{eff}$ and the substituent constants[78]. Combining the Hammett equation with the relation (28), we then obtain

$$\rho\sigma = \lg\frac{k_{eff}}{k_{0\,eff}} + \lg\frac{K_2}{K_{02}} + \lg\frac{(1 + K_1/h_0 + h_R/K_2)}{(1 - K_{01}/h_0 + h_R/K_{02})}. \qquad (38)$$

The last term on the right-hand side of (38) can be neglected, since in 99.9% sulphuric acid $K_1 \ll h_0$ and $K_2 \gg h_R$. If the rate constants of the reactions of substituted benzoic acids with hydrogen azide and the equilibrium constants K_2 correlate with the same substituent constants σ^+, we then have

$$\lg\frac{k_{eff}}{k_{0\,eff}} = (\rho_1 - \rho_2)\,\sigma^+. \qquad (39)$$

A correlation is indeed observed between $\lg k_{eff}$ and σ^+ (Fig. 3), and the equation to the regression line is

$$\lg k_{eff} = -(2.33 \pm 0.15)\,\sigma^+ + (1.21 \pm 0.07), \qquad (40)$$

$$r = 0.99;\ n = 7;\ s = 0.11.$$

However, the constant obtained in this way is an effective value, and it is difficult to assess the reaction mechanism from its sign and absolute magnitude.

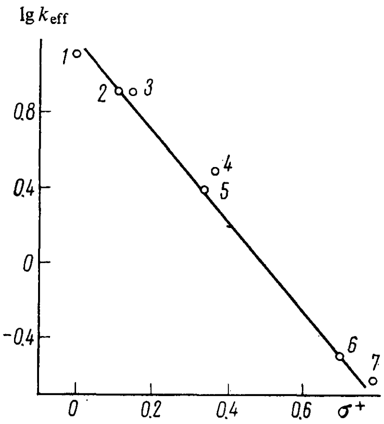


Figure 3. Dependence of effective reaction rate constants for benzoic acids on substituent constants σ^+ (for numbering of points see Table 6).

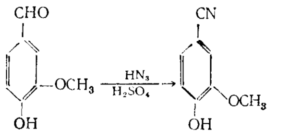
The correlation (40) indicates that the rate constants k_1, k_{-1}, and k_3 are not comparable, and that the rate of the reaction of substituted benzoic acids with hydrogen azide is increased by the presence of electron-donor substituents. Yet the opposite pattern is found for the analogous reactions of ketones and aldehydes, when addition of hydrogen azide to the protonated carbonyl compound is the rate-determining stage[64,65]. Furthermore, the tendency of substituted phenyl groups to migrate in reactions involving rearrangement of the carbon skeleton increases in the presence of electron-donor substituents[79,80]. These results obviously indicate that the rearrangement (*e*) is the rate-determining stage in the reaction of benzoic acids with hydrogen azide. The same conclusion was reached by Rabinowitz et al.[81], who found an approximately 15% decrease in reaction velocity when the carbonyl carbon-12 atom in carboxylic acids was replaced by carbon-14. This is supported by the absence of a kinetic isotope effect for the reaction of benzoic acids[70] in D_2O–D_2SO_4 relative to the H_2O–H_2SO_4 system of the same composition (79.3%): k^D_{eff} and k^H_{eff} are respectively 0.027 and 0.035 $M^{-1}\,min^{-1}$. Some difference between these constants is obviously due to differences in the value of D_0 and H_0 [82,83] and in the basicity constants of hydrogen azide in deuterosulphuric[56] and sulphuric[55] acids. The opposite kinetic isotope effect is found for the reaction of ketones and aldehydes with hydrogen azide: k^D/k^H = 4-6.[23,84]

III. APPLICATIONS OF REACTION

The reaction of aldehydes with hydrogen azide-provides a simple method for obtaining formamides and nitriles. However, several manuals of organic synthesis[85] state that it is difficult to control the proportions of the products. Actually, the factors governing the ratio of formamide to nitrile have become known only after the reaction mechanism has been finally established. This reaction can now be expected to be an effective method for obtaining various formamides and nitriles. It is noteworthy that the Schmidt reaction enables nitriles to be obtained from readily available compounds in a single stage, with sulphuric acid as catalyst. This method has advantages over others, since in most cases metal cyanides are used to obtain nitriles, or else the reaction occurs in several stages.

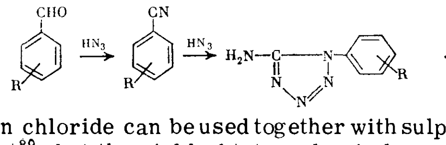
With acetaldehyde hydrogen azide forms acetonitrile[86]. This is apparently the only example of the application of the Schmidt reaction to aliphatic aldehydes. Such a situation is obviously due to their instability in aqueous sulphuric acid.

Aromatic aldehydes have been studied in greater detail. Thus McEwen et al.[59] investigated the action of hydrogen azide on a series of substituted benzaldehydes in the presence of sulphuric acid. They showed that the yields of formamides and nitriles can vary within wide limits depending on the acid concentration. From 4-hydroxy-3-methoxybenzaldehyde[87] the corresponding nitrile was obtained in 70% yield:



(41)

With excess of hydrogen azide and substituted benzaldehydes in the presence of concentrated sulphuric acid 5-amino-1-aryltetrazoles are formed[88,89]:

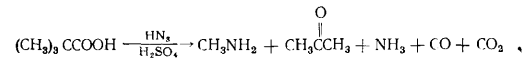


(42)

In this case tin chloride can be used together with sulphuric acid as catalyst[89], but the yield of tetrazoles is lower.

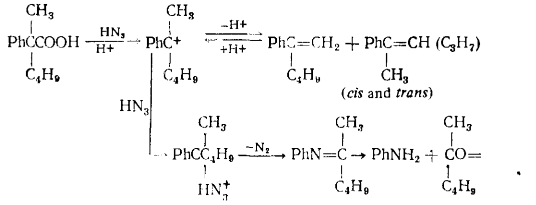
Since the early work of Schmidt the reaction of carboxylic acids with hydrogen azide has been widely used as a convenient method for obtaining various amines. This is due to the advantage of the Schmidt reaction over other processes for obtaining amines, e.g. the related Curtius and Hofmann rearrangements, as it occurs in a single stage. Other advantages are its simplicity, the availability of the initial reactants, and the quite mild conditions. The catalysts may be sulphuric acid[4,70,73], polyphosphoric acid[90,91], and mixtures of sulphuric and trichloroacetic acids[92,93] and of trifluoroacetic acid and anhydride[75]. In most cases sulphuric acid is used. Hydrogen azide is used as a solution in an inert solvent[74,94] (chloroform, benzene) or is generated *in situ* by adding sodium azide to the reaction mixture[95-97]. The latter procedure eliminates contact with the explosive and toxic hydrogen azide without lowering the yield of products. Aliphatic[98-100], alicyclic[3,74,94,101], bicyclic[102], and aromatic[4,103-106] acids react with hydrogen azide. The presence of a heteroatom (boron, nitrogen, oxygen) in the acid molecule[9,10,101,107] does not hinder the normal course of the reaction.

Aliphatic carboxylic acids of normal structure are converted into good yields of the corresponding amines[98]. However, acids containing alkyl or aryl substituents in the α position undergo secondary reactions. For example, αα-dimethylpropionic ("trimethylacetic") acid[108] forms a mixture of several products:



$$(CH_3)_3CCOOH \xrightarrow[H_2SO_4]{HN_3} CH_3NH_2 + CH_3\overset{\overset{O}{\|}}{C}CH_3 + NH_3 + CO + CO_2\ ,$$

A similar pattern is observed with 2-methyl-2-phenylhexanoic acid[91,109]. These departures from the "normal" reaction are due to decarboxylation of the initial acid to the corresponding carbocation and its subsequent reactions:

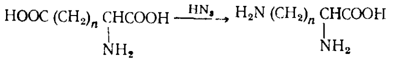


(43)

In aliphatic dicarboxylic acids only one carboxyl reacts if it is separated from the other by less than two carbon atoms[99]:

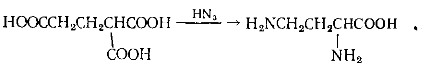
$$HOOCCH_2COOH \xrightarrow{HN_3} H_2NCH_2COOH\ . \qquad (44)$$

In the case of amino-dicarboxylic acids hydrogen azide reacts with the carboxyl that is more remote from the amino-group[99]:



$$HOOC(CH_2)_n\underset{\underset{NH_2}{|}}{C}HCOOH \xrightarrow{HN_3} H_2N(CH_2)_n\underset{\underset{NH_2}{|}}{C}HCOOH\ . \qquad (45)$$

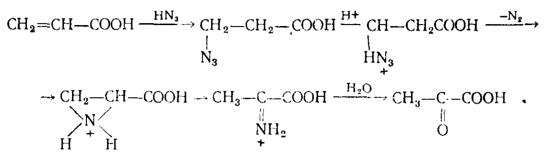
Similarly, tricarboxylic acids yield diamino-carboxylic acids[100]:



$$HOOCCH_2CH_2\underset{\underset{COOH}{|}}{C}HCOOH \xrightarrow{HN_3} H_2NCH_2CH_2\underset{\underset{NH_2}{|}}{C}HCOOH\ . \qquad (46)$$

Tetracarboxylic acids are converted into the corresponding tetramines[110].

Unsaturated aliphatic acids such as acrylic undergo a complicated reaction yielding pyruvic acid[111]:

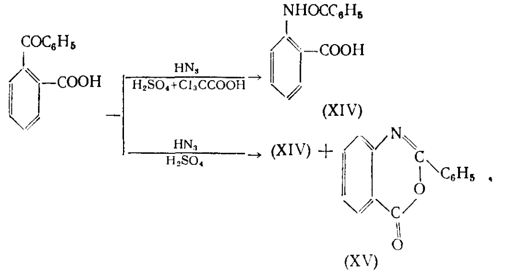


(47)

As already noted, alicyclic and bicyclic mono- and dicarboxylic acids react with hydrogen azide to form the corresponding amines, unaccompanied by *cis–trans* isomerisation. Thus the Schmidt reaction has been used to obtain *cis*- and *trans*-cyclobutane-1,2-diamines[74] and *cis*-cyclohexane-1,2-diamine[6,7].

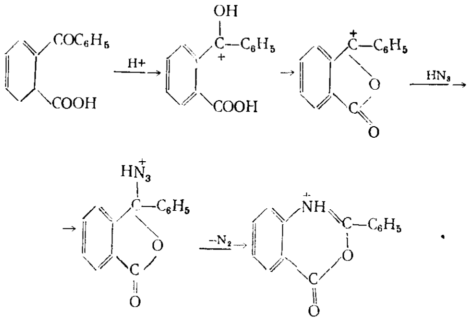
The Schmidt reaction with aromatic carboxylic acids has been especially widely studied. Thus substituted benzoic acids[4,103-106] are converted by hydrogen azide in the corresponding anilines in good yields. If electron-accepting substituents are present in the benzoic acids, 100% sulphuric acid[105] or even oleum[103,106] must be used as catalyst.

Interesting results were obtained with *o*-benzoylbenzoic acid[92,93]. If a mixture of sulphuric and trichloroacetic acids is used as catalyst, benzanilide (XIV) is formed, but with concentrated sulphuric acid as catalyst this is accompanied by oxazine (XV):



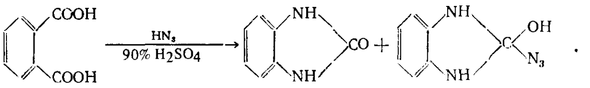
(48)

Oxazine results from cyclisation and ring expansion:



(49)

Aromatic dicarboxylic acids have been less studied than benzoic acids. In the presence of concentrated sulphuric acid phthalic acid gives an 80% yield of anthranilic acid with traces of *o*-phenylenediamine[4]. If 90% sulphuric acid is used, a mixture of two products—benzimidazolinone and 2-azido-2-hydroxybenzimidazoline—is formed[112]:



(50)

The information given in the present Review on the reactions of aldehydes and carboxylic acids with hydrogen azide indicates the considerable progress made in this field. Future research will undoubtedly bring interesting knowledge on the mechanism of acid-catalysed rearrangements and reveal fresh opportunities for the application of these reactions to organic synthesis.

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Poly(arylene Sulphides)—Preparation, Structure, and Properties

V.A.Sergeev, V.K.Shitikov, and V.I.Nedel'kin

Chemical aspects of the synthesis, structure, and properties of oligo- and poly-(arylene sulphides) are surveyed. The Review concludes with several fields of application and a list of 252 references.

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II. Methods of preparation of poly(arylene sulphides) 1095

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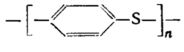
I. INTRODUCTION

The advantageous properties of polymers like polyphenylenes are difficult to realise practically in ready-made materials and articles, mainly because such polymers are insoluble and infusible right up to their thermal decomposition temperatures. As a consequence, vigorous research has been undertaken on the synthesis of modified polymers of this type. A great deal of experimental information has now accumulated on the synthesis and the properties of oligo- and poly-phenylenes containing functional groups[1], whose fields of practical application are continuously expanding. Polyheteroarylenes, containing in the main chain aromatic rings and various heteroatoms, e.g. oxygen[2] or sulphur[3], are being increasingly utilised in industry. Recent years have seen an especially marked increase in the number of studies aimed at developing methods of preparation, investigating the properties, and applying poly(arylene sulphides), which are distinguished by high resistance to thermal oxidation and several specific properties.

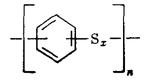
Although poly(arylene sulphides) were first synthesised in 1866, by the action of alkali-metal sulphides on bis-diazonium salts of benzidine[4], systematic investigations on their synthesis and more thorough study of their structure and properties in 1948, after Macallum's discovery[5] of a new process for obtaining poly(arylene sulphides) by the high-temperature polycondensation of polyhalogenated benzenes in the presence of mixtures of sulphur and alkali-metal carbonates.

Methods for obtaining oligo- and poly-(phenylene sulphides) of linear structure



have been elaborated in the greatest detail, and their properties have been investigated most thoroughly. The enhanced heat-resistance and thermal stability of such polymers is due primarily to the comparatively high energy of rupture of the phenyl–sulphur bond (72.7 kcal mole^{-1})[6] and to their physical structure, largely determined by the strong intermolecular interaction of the polymer chains and the formation of a crystalline structure[7]. Furthermore, the presence of sulphur atoms between aromatic rings not only ensures that the polymeric molecule shall be flexible and highly resistant to thermal oxidation but also is responsible for the cross-linking of poly(phenylene sulphides) at 300–350°C.[8,9]

The term *poly(arylene sulphides)* is met more often than other names, in both Soviet and foreign literature, in relation to simple aromatic "polythioethers" or polysulphides. The Reviewers consider this name most rational and able to represent quite adequately the various chemical structures of most oligomers and polymers of simple aromatic polysulphides. For example, the name *poly(phenylene sulphides)* applies to polymers in which the repeating monomer unit is



where $x = 1$. The aromatic rings in such polymers may be combined by sulphur atoms in the relative positions 1,2, 1,3, and 1,4 (poly-(*o*-phenylene sulphide), poly-(*m*-phenylene sulphide), and poly-(*p*-phenylene sulphide) respectively). When $x \geqslant 2$, poly(phenylene disulphides), poly(phenylene trisulphides), poly(phenylene tetrasulphides), and poly(phenylene polysulphides) are formed.

The same principles underly the nomenclature of poly(arylene sulphides) having a branched structure or substituents in the aromatic ring. The only difference is that the substituents and their positions are indicated before the name of the chief arylene ring. For example, a polymer based on the monomer unit

is termed *poly-(2,6-dimethyl-1,4-phenylene sulphide)*.

The present Review surveys almost all known methods for obtaining poly(arylene sulphides) of diverse structure. It gives their principal characteristic properties and several fields of application.

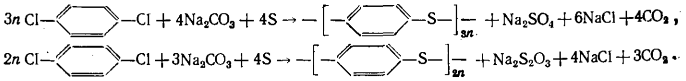
II. METHODS OF PREPARATION OF POLY(ARYLENE SULPHIDES)

1. Polycondensation of Polyhalogenated Aromatic Compounds with a Mixture of Sulphur and Various Derivatives of Alkali and Alkaline-earth Metals

One of the best known and simplest methods for obtaining poly(phenylene sulphides) is based on the high-temperature (275–360°C) polycondensation of polyhalogenated benzenes in the presence of mixtures of sulphur and alkali-metal carbonates, first accomplished in 1948 by Macallum[5]. In his view only after a first stage of formation of alkali-metal sulphides

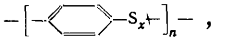
$$3M_2CO_3 + (2n + 2)\,S \rightarrow 2M_2S_n + M_2S_2O_3 + 3CO_2$$
$$4M_2CO_3 + 4S \rightarrow 3M_2S + M_2SO_4 + 4CO_2$$

did polycondensation occur with the halogenobenzenes. With *p*-dichlorobenzene mixed with sulphur and sodium carbonate we can represent the process by the equations



The poly-(*p*-phenylene sulphides) thus obtained are slightly coloured powders, sparingly soluble in the usual organic solvents and softening at 250–300°C. Macallum assumed[10] that the first stage was far slower than the second, so that the reaction mass always contained a small quantity of elementary sulphur, which assists polycondensation of halogenobenzenes with metal sulphides. Indeed, it was found experimentally[5] that a slight excess of elementary sulphur not only played a part in building up the polymer chain but also catalysed the process to high degrees of conversion of the initial halogenobenzenes. In the absence of excess of sulphur halogenated aromatic compounds and alkali-metal sulphides either do not interact at all or undergo polycondensation only slowly even at high temperatures.

However, the quantity of combined sulphur depends mainly on the initial molecular ratio of the dihalogenobenzene and sulphur[10], so that the monomer unit in the resulting poly-(*p*-phenylene sulphides) can be represented by the general formula



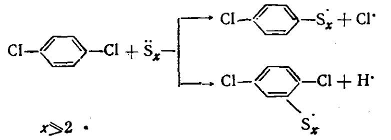
Thus the polycondensation of *p*-dichlorobenzene and sulphur taken in the molecular proportions 1.0 : 1.5 yielded solid poly-(*p*-phenylene sulphides) of m.p. 215–240°C, whose monomer unit corresponded to the above general formula with $x = 1$. When the molecular ratio was increased from 1.5 to 2–3 the melting point fell to 55–80°C, while the sulphur content corresponded to $x = 2$–5. Copolymers obtained from a mixture of *p*-di- and 1,2,4-tri-chlorobenzenes in the presence of sulphur and sodium carbonate had the analogous structure

$$-[C_6H_4S_x]\cdot[-C_6H_3S_y]_n-$$

with $x = 1.15$–1.25, $y = 1.72$–1.87, and $n = 0.04$–0.25. From the above results it was concluded[10] that the main polymer molecule consisted of aromatic rings linked both by monosulphide and by polysulphide groups.

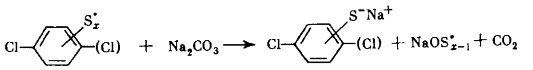
Later investigations have shown[11] that the polycondensation of dihalogenobenzenes can be accomplished also in the presence of a mixture of sulphur and an alkaline-earth metal or its carbonate, borate, or oxide. The formation of poly-(*p*-phenylene sulphides) is catalysed by *N*-halogenated derivatives, e.g. *N*-bromosuccinimide, *N*-bromoacetamide, etc. (5% based on the initial monomers)[12]. Aromatic compounds containing activated halogen atoms, e.g. di-*p*-chlorophenyl sulphide or sulphone, have been used[13] as activators of polycondensation: in their presence up to 80% yields have been obtained of poly(arylene sulphides) of molecular mass 237 000 (calculated from the chlorine content).

Lenz and Carrington[14] suggested an alternative mechanism, in which the first stage involves reaction between the halogenated aromatic compound and a sulphur biradical formed during heating:

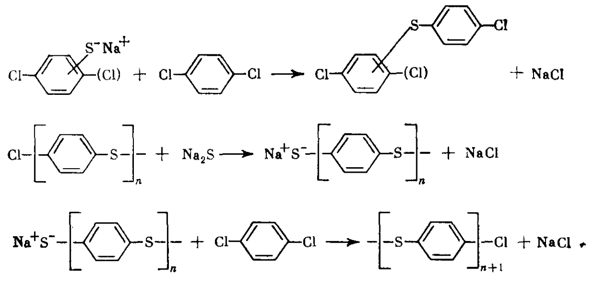


$x \geqslant 2$.

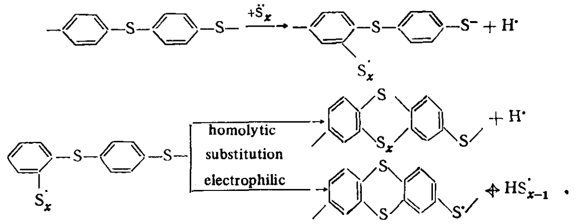
The polysulphide substituents in the aromatic ring then react with sodium carbonate to form benzenethiolate ions:



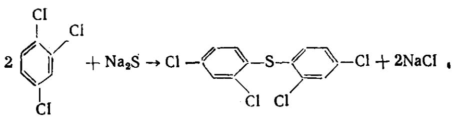
Nucleophilic substitution occurs with the dihalogenoarenes to give primary oligomeric or secondary polymeric products:



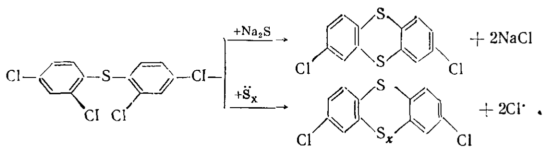
According to the above scheme sulphur biradicals are able to replace not only halogen but also hydrogen atoms in the aromatic ring, which may promote the formation both of branched and of "cross-linked" poly(arylene sulphides). Indeed, infrared spectroscopy established[15] that the polymer obtained from *p*-dichlorobenzene had a branched or partly cross-linked structure. Some ordering (detected by X-ray diffraction) was attributed[15] to the presence of linear segments comprising 6 or 7 monomer units between side-chains, able to form zones with some ordering of the spatial arrangement of the polymer chains. The increase in the sulphur content of the polymer above that calculated for a $C_6H_4.S$ monomer unit was explained[15] by intramolecular cyclisation, which may result in sulphur-containing rings:



Study of the simultaneous polycondensation of *p*-di- and 1,2,4-tri-chlorobenzenes revealed[15,16] not only that the rate of nucleophilic substitution of the latter exceeds that of the former more than fourfold but also that the 1-chlorine atom in the trichlorobenzene is the most reactive of the three in nucleophilic substitution. Therefore the first stage involves preferential formation of a dimer from 1,2,4-trichlorobenzene:



Subsequent nucleophilic or radical substitution of one of the *ortho*-chlorine atoms forms phenylthio-groups or polysulphide links, which are readily converted by intramolecular cyclisation into thianthren units:



Hence, owing to intramolecular cyclisation, 1,2,4-trichlorobenzene is actually difunctional on polycondensation in the presence of sulphur and alkali-metal carbonates. The change in functionality during copolycondensation and the considerable differences in activity between the initial monomers have a significant influence on the direction of the process and on the properties of the resulting poly(phenylene sulphides).

Table 1. Properties of homopolymer from *p*-dichlorobenzene and of copolymer from *p*-di- and 1,2,4-tri-chlorobenzenes.

Property	Homopolymer*	Copolymer**
1	2	3
Degree of conversion (from Cl⁻ in aq. extract), %	99.0	99.0
Yield of toluene-soluble polymer, %	8.3	5.8
Softening point, °C	166—171	166—171
Sulphur content, %	35.1±0.4	31.5±0.3
Chlorine content, %	1.60±0.1	1.70±0.1
Yield of polymer soluble in diphenyl ether, %	63.5	77.5
Softening point, °C	193—204	171—177
Sulphur content, %	33.2±0.3	31.6±0.3
Chlorine content, %	0.50±0.1	0.6±0.1
Yield of insoluble polymer, %	20.6	11.6
Total yield, %	94.2	94.9

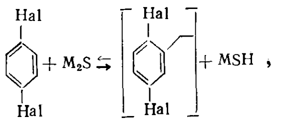
*Molecular proportions $C_6H_4Cl_2 : S : Na_2CO_3 = 1 : 1.73 : 1.73$ at 300°C for 20 h.

**Molecular proportions $C_6H_4Cl_2 : C_6H_3Cl_3 : S : Na_2CO_3 = 1 : 0.1 : 1.84 : 1.84$ at 300°C for 24 h.

Table 1 compares the characteristics of the homopolymer obtained from *p*-dichlorobenzene with those of the copolymer obtained from the same monomer together with 10 mole % of 1,2,4-trichlorobenzene[15]. It is evident that polycondensation gives high yields of poly(phenylene sulphides), and higher yields of soluble fractions in the case of the copolymer. However, the strength characteristics of the copolymers are somewhat inferior to those of the homopolymers. In order to improve the durability of copolymers it was suggested[16] that copolycondensation with sulphur and sodium carbonate should be conducted in the presence of alkylated aromatic hydrocarbons, e.g. toluene, xylene, methylnaphthalenes, etc., which were considered to inhibit or completely to eliminate formation of thianthren groups in the copolymer structure.

Intramolecular cyclisation can be observed especially distinctly in the high-temperature polycondensation of *o*- and *m*-dihalogenobenzenes in the presence of a mixture of sulphur with oxides or sulphides of alkali or alkaline-earth metals. . Thus under these conditions up to 75% yields of thianthren were obtained from *o*-dichlorobenzene[10], but from *m*-dichlorobenzene an insoluble product was formed and a substance was isolated (molecular mass 1120) that contained 31.5% of sulphur and was free from chlorine[17]. It was considered[17] that the polycondensation of *o*- and *m*-dihalogenobenzenes may give high yields of cyclic *ortho*- or *meta*-substituted oligomers (tetramers, pentamers, heptamers, nonamers, decamers, etc.).

The evolution of hydrogen sulphide under these conditions of the Macallum polycondensation of dihalogenobenzenes was attributed to side-reactions with the metal sulphide[14]:



$$2MSH \rightleftarrows M_2S + H_2S$$

This process results in formation of polymers having a branched and cross-linked structure.

Monohalogenated aromatic compounds containing various substituents in the aromatic ring can also be used for high-temperature polycondensation with sulphur and sodium carbonate[18,19]. Thus various poly(phenylene sulphides) have been obtained by heating *para*-halogenated phenols, toluene, aniline, or benzoic acid with a mixture of sulphur and sodium carbonate (molecular proportions 1 : 1.73 : 1.73) at 160–340°C for 18 h. The degree of conversion of the monomers, calculated from the quantity of chloride ions in an aqueous extract, depends on their structure and on the temperature of polycondensation; the yield of the reaction products reaches 80% or more. Experimental results are given together with the polymer structure established on the basis of infrared, ultraviolet, and nuclear magnetic resonance spectral data[18]. For comparison polymers were obtained from *p*-dichlorobenzene under the same conditions. Poly(phenylene sulphides) obtained from *para*-chlorinated phenol and aniline contain hydroxy- and amino-groups respectively, whereas the carboxyl and methyl groups of *para*-chlorinated benzoic acid and toluene undergo various changes during polycondensation. On the assumption of first- or second-order kinetics for polycondensation, with simultaneous solution of the Arrhenius and Hammett equations, it was found that the overall rate depended mainly on polar effects and on the slowest stage, i.e. electrophilic attack by the sulphur atom on the monomer. Raising the temperature of polycondensation increases the yield of polymers having a branched and cross-linked structure.

Scanning calorimetry and thermogravimetric analysis indicate[19] that poly(phenylene sulphides) containing various substituents in the aromatic ring have softening and decomposition points of 90–263 and 270–320°C respectively. The degradation of such polymers has first-order kinetics; activation energies in an atmosphere of nitrogen are 7–30 kcal mole^{-1}, the lowest values applying to poly(phenylene sulphides) containing amino- and hydroxy-groups.

According to a patent[20] soluble poly(phenylene sulphides) resistant to thermal oxidation at high temperatures can be obtained from a mixture of *para*-chlorinated triphenyl-1,3,5-triazines with *p*-dichlorobenzene. When such monomers undergo polycondensation in the presence of a mixture of sulphur with carbonates, sulphides, or oxides of alkali or alkaline-earth metals at 270–360°C, triazine-containing poly(phenylene sulphides) are obtained that undergo losses in mass of 3.3% and 5.3% when heated at 300°C for 100 h and at 400°C for 20 h respectively.

Aromatic polysulphide polymers of molecular mass M_n = 2500–10 000) and general formula $[ArS_x]_n$, where $x = 2-5$, which form predominantly white powders soluble in oxolan and with m.p. $\geqslant$100°C, have been obtained by the polycondensation of disulphonic, disulphinic, dithiosulphonic, and dithiosulphinic acids, and also their salts, esters, anhydrides, chlorides, and amides, with alkali-metal polysulphides formed by the action of powdered sulphur on aqueous solutions of alkali-metal sulphides[21]. Water or a lower alcohol was used as solvent, and polycondensation was effected in the presence of gaseous hydrogen together with sulphides or polysulphides of elements of the iron subgroup, as well as the finely powdered metals, under 7–350 kg cm^{-2} in an autoclave at 150–200°C.

2. Polycondensation of Polyhalogenated Aromatic Compounds with Alkali-metal Sulphides

Despite the apparent simplicity and the availability of the initial compounds, the high-temperature polycondensation of polyhalogenoarenes in the presence of a mixture of sulphur and a carbonate, sulphide, or oxide of an alkali or an alkaline-earth metal has not found wide industrial application owing to the experimental difficulties involved in isolating the poly(phenylene sulphide) from the melt containing a large quantity of impurities of low molecular weight and owing to the strongly branched and partly cross-linked character of the products. These disadvantages are to some extent avoided when polyhalogenated aromatic compounds undergo polycondensation with alkali-metal sulphides in polar organic solvents of high boiling point[22,23].

Polycondensation of polyhalogenated aromatic compounds with alkali-metal sulphides is at present the only industrial method of obtaining poly(arylene sulphides)[24], but information on this process is extremely limited. Polycondensation is continued in an inert atmosphere at 125–450°C for 17–20 h; *N*-methylpyrrolid-2-one, hexamethylphosphoramide, tetramethylurea, etc. can be used as solvents. Poly(phenylene sulphides) of highest molecular mass are obtained in *N*-methylpyrrolidone solution[22]. At moderate temperatures and pressures maximum rates can be achieved[25] by gradually adding increasing quantities of the arylene halide to the alkali-metal sulphide and varying the duration of polycondensation. The anhydrous sulphide (mainly sodium sulphide) is generally used, or else water of crystallisation is evaporated from a hydrate by preheating the reaction mass to 160°C.[22,26] Alternatively, sodium sulphide can be obtained directly in the reaction vessel by treating sodium hydroxide with hydrogen sulphide[27,28] or industrial waste gases containing it[29].

Isolation of the poly(arylene sulphides) from the reaction mixture apparently presents some difficulty. For this purpose it is proposed to treat the mixture with water vapour[30] or liquid ammonia[31] under pressure, evaporate off the solvent under adiabatic conditions[32–35], or apply filtration followed by treatment of the polymer with water and organic solvents[36]. The extractants used are acyclic or alicyclic hydrocarbons[37], dichloroethane, or benzene[38].

Yields up to 85% of poly(arylene sulphides) have been obtained in this way. The products were pale grey powders, soluble in high-boiling organic solvents, e.g. polyphenols, above 235°C.[39] Poly(arylene sulphides) obtained from *p*-dihalogenobenzenes and sodium sulphide in *N*-methylpyrrolid-2-one solution have molecular masses around (5–14) $\times 10^3$. Such products probably separate from solution during polycondensation, and play no part in further growth of the polymer chain.

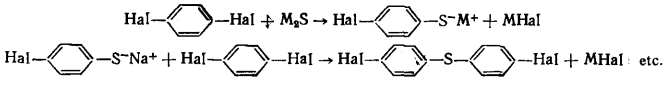
Table 2. Dependence of viscosity of poly(arylene sulphides) (melt at 303°C) on initial molecular ratio of *p*-dichlorobenzene to sodium sulphide.

Ratio	Viscosity, P	Ratio	Viscosity, P
1:1	37.3	1.04:1	4.8
1.02:1	6.4	1.05:1	7.1

The molecular mass is also influenced by the properties of the initial components[22]. Table 2 gives the viscosities of the poly(arylene sulphide) melts obtained with different initial molecular ratios of *p*-dichlorobenzene and sodium sulphide[22]. The use of purified initial compounds, including sodium sulphide with an impurity content not exceeding 1–2%, is therefore of interest[28,41]. An equimolecular mixture of purified *p*-dichlorobenzene and sodium sulphide gave poly(phenylene sulphides) having a lower melt index and a higher viscosity. With a 2 : 1 molecular ratio of sodium sulphide oligo(phenylene sulphides) were obtained having molecular mass 510 and softening point 125–130°C.[27] Benzenethiol separated as a byproduct in yield almost equal to that of the oligomers. If, however, a threefold excess of functional groups in the halogeno-derivative was used relative to the sodium sulphide, a product of low molecular mass was obtained[42], with a mean degree of polycondensation of 2.

Thus the above results show that equimolecular proportions of the initial components are necessary to obtain poly(arylene sulphides) of maximum molecular mass. Furthermore, there are data indicating that two measures must be taken to increase the rate of the process and the molecular mass of the products: (i) polycondensation of sodium sulphide with dihalogenated unsaturated cyclic hydrocarbons, preferably aromatic, in the presence of trihalogenobenzenes[22,28] or 3–33 wt.% of activators (a mixture of oligo(phenylene sulphides) extracted from products of a similar reaction with benzene, toluene, or *N*-methylpyrrolidone at 80–150, 110–150, or 135–150°C respectively)[43,44]; and (ii) the temperature must be raised at a specified rate during polycondensation[45].

According to infrared and n.m.r. spectral data and X-ray diffraction poly(arylene sulphides) obtained by the polycondensation of dihalogenated aromatic compounds with alkali-metal sulphides have a linear structure, in contrast to the branched polymers obtained in the presence of sulphur and alkali-metal carbonates. It follows that a mechanism of nucleophilic substitution is responsible for the appearance of the former when the process occurs in a polar organic solvent[40]:



Various halogenated aromatic compounds can be used for polycondensation with sodium sulphide in order to obtain poly(arylene sulphides) having modified properties.

Thus the copolycondensation with sodium sulphide of *p*- and *m*-dichlorobenzenes in various proportions by weight gives poly(phenylene sulphides) that are soluble in oxolan[46], a few characteristics of which are listed in Table 3. It is significant that increase in the proportion of *p*-dichlorobenzene in the reaction mixture increases the viscosity and raises the glass point of the resulting polymers. Unfortunately, however, the patent literature contains no evidence of their structure[46].

Table 3. Properties of copolymers from *p*- and *m*-dichlorobenzenes.

Isomer, %		Properties of copolymers		
para	*meta*	η	glass point, °C	solubility in oxolan, g/100 g
75	25	0.11	68	insol.
50	50	0.09	49	>20
25	75	0.05	47	42
0	100	0.01	15	<0.5

Polycondensation of a mixture of poly-(*m*- and *p*-phenylene sulphides) with sodium sulphide yields block copolymers[47] containing, according to infrared spectroscopy, *meta*- and *para*-substituted aromatic groups in proportions varying between the limits 3 : 1 and 1 : 3 for fractions of the block copolymer respectively soluble and insoluble in *N*-methylpyrrolidone.

Polymethylated and branched poly(phenylene sulphides) have been obtained respectively from dibromodurene and from a mixture of *p*-dibromobenzene and 1,3,5-tri-*p*-bromophenylbenzene in the molecular proportions 20 : 1.[40] The good solubility of the products in dimethylformamide is attributed[40] to disorder resulting from the introduction of substituents or a branching agent respectively into the polymer molecule. In contrast to the poly(phenylene sulphide) obtained from *p*-dibromobenzene and melting at 280°C, the copolymer from the 20 : 1 mixture with 1,3,5-tri-*p*-bromophenylbenzene softened at around 235°C.

Poly(arylene sulphides) containing reactive groups can be obtained by the polycondensation with alkali-metal sulphides of halogenated aromatic compounds containing various functional groups. Thus 2,5-dichloroaniline yields amino-containing polymers, which become infusible and insoluble on treatment with dicarboxylic acids[43], but the corresponding products of the simultaneous polycondensation of *p*-dichlorobenzene and *o*-chloroaniline melt at 283–286°C and have a viscosity of 52 P at 303°C.[22] Poly(arylene sulphides) from 2,4-dichlorotoluene soften below 100°C and are readily soluble in benzene, while those from 2,5-dichlorobenzenesulphonic acid are readily soluble in water[22].

The polycondensation of *p*-dichlorobenzene with sodium sulphide in the presence of copper cyanide gives oligo-(phenylene sulphides) of molecular mass 500–5000, containing terminal nitrile groups[48], which may subsequently be involved in thermal or catalytic cross-linking.

Polycondensation of dichlorodinitrobenzene with sodium tetrasulphide at 70 and 110°C gives oligo(phenylene tetrasulphides) containing amino- and nitro-groups[49], the maximum yield of polymer (>90%) being obtained with the reactants in the molecular proportions 1 : 2. This is attributed mainly to secondary processes, in particular reduction of nitro- to amino-groups:

$$C_6H_2Cl_2(NO_2)_2 + 2Na_2S_4 + 2H_2O \rightarrow C_6H_2Cl_2(NH_2)_2 + 2Na_2S_2O_3 + 4S\ .$$

Since the content of so called free sulphur in the polymer is only 0.78%, while the total sulphur content is ~44.2%, it is thought[49] that all the sulphur atoms are present in the main chain of the macromolecule, while the terminal groups may be chlorine atoms or hydroxyls (analysis indicates that the latter amount to 1.93%). Apparently, therefore, the structure of the oligomer can be represented by the formula

$$Cl\,(NH_2)_2\,C_6H_2S_4\text{—}\ldots\text{—}C_6H_2\,(NH_2)_2\,OH.$$

The maximum molecular mass is ~850 (determined cryoscopically in benzene). The resulting oligomers had softening points of 47–63°C and were readily soluble in benzene, acetone, carbon disulphide, and mineral acids.

Another monomer that has been used is di-*p*-chlorophenyl sulphone, whose chlorine atoms are activated by the electron-accepting sulphonyl group[50–52]. In dimethyl sulphoxide solution at 170°C a theoretical yield was obtained of polymers having a reduced viscosity of 0.15 in a 1% solution in this solvent at 25°C. Polycondensation of the initial sulphone with sodium sulphide can be effected also in aqueous solution or in a mixture of an organic solvent with water at 150–400°C.

Poly(quinone sulphides) of molecular mass ~3000 have been obtained by the polycondensation of tetrachloro-*p*-benzoquinone with sodium sulphide in toluene solution at 0°C.[53] They are solid powders apparently having a linear structure, with softening points of 320°C and above.

Quite recently poly(arylene sulphides) have been obtained by heating polyhalogenated aromatic compounds with thiourea and oxides (or carbonates) of alkali and alkaline-earth metals in *N*-methylpyrrolidone solution under pressure[54]. The procedure is to heat thiourea with the metal oxide (or carbonate) in *N*-methylpyrrolidone solution, and then add to the mixture the polyhalogenated aromatic compound, which probably reacts with an already formed sulphide. Yields of 41–94% are obtained of polymers that soften at 249–273°C and have reduced viscosities of 0.01–0.07.

The thiourea can be replaced by thiocarbonates of general formula R_2CS_3 (where R represents an alkali metal or a hydrocarbon radical)[55–57], thiosulphates, thiocarboxylic acids[57–59], thiols, thiolates, or sulphides containing an activating substituent in an α or β position (e.g. α-mercaptopropionic acid)[57,60], carbon disulphide and carbonyl sulphide[61], thioamides of general formula $R'(CS.NR_2)_x$ (where R is hydrogen or a radical of valency 1–4), *N*-methylpyrrolidine-2-thione[62], thiocarbamates (e.g. sodium dimethyldithiocarbamate)[63], and also phosphorus pentasulphide[64] in hexamethylphosphoramide solution.

Yields of poly(phenylene sulphides) from the polycondensation of dihalogenated aromatic compounds with alkali-metal hydrogen sulphides are only 24–45%.[65] To increase the yield the polycondensation is conducted in the presence of alkali-metal *N*-substituted ω-amino-carboxylates[66]. Similar compounds have been used also in the polycondensation of dihalogenated aromatic compounds with carbon disulphide[67]. Furthermore, up to 94% yields of poly(phenylene sulphides) are obtained from dihalogenated aromatic compounds and alkali-metal hydrogen sulphides in the presence of alkaline-earth metal hydroxides or alkali-metal carbonates[68] or of sodium hydroxide and salts of aliphatic alcohols and acids[69].

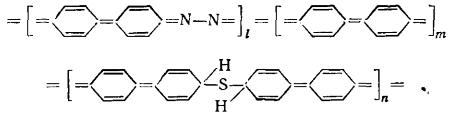
3. Decomposition of Diazonium Salts

Poly(arylene sulphides) were first obtained by Griess[4] in 1866, by the decomposition of aromatic diazonium salts in the presence of an alkali-metal sulphide. An equation has been suggested for this reaction only comparatively recently[70]:

$$n\overline{\mathrm{Hal}}\overset{+}{\mathrm{N}}_2\mathrm{Ar}\overset{+}{\mathrm{N}}_2\overline{\mathrm{Hal}} + nM_2S \rightarrow -[-\mathrm{ArS}-]_n- + 2n\mathrm{MHal} + 2nN_2 .$$

Later work has shown that decomposition takes place also in the presence of hydrogen sulphide[17] or thiourea[7] and water at 0–5°C. The products (obtained in almost theoretical yield) are brown powders, partly soluble in carbon disulphide, dioxan, and dimethylformamide. The soluble fraction of the poly(arylene sulphides) softens at 70–80°C, but the insoluble fraction does not soften below the thermal decomposition point.

Since cryoscopic determination in diphenylamine solution and calculation from the chlorine content give molecular masses of 460–1400 and 5000–10000 respectively for the soluble fraction, it is assumed[72] that chlorine atoms are present in the polymer molecule not only as terminal groups. Elementary analysis and the ultraviolet spectra indicate[70] that the polymer chain contains quinoid structures, azo-groups, and sulphur in semiquinoid groupings:



The presence of azo-groups is confirmed also by the evolution of gaseous nitrogen when the soluble fraction is heated to 150–200°C, with formation of an infusible and insoluble product.

The formation of azo-groups in the polymer molecule may result from the decomposition of aromatic diazonium salts by a radical mechanism:

$$\overset{+}{\mathrm{N}}_2\mathrm{Ar}\overset{+}{\mathrm{N}}_2 \xrightarrow{\mathrm{HS}^-} {}^{\cdot}\mathrm{N}_2\mathrm{Ar}^{\cdot} + \ddot{\mathrm{Ar}} + {}^{\cdot}\mathrm{N}_2\mathrm{ArN}_2^{\cdot} + \ddot{\mathrm{S}} \rightarrow -[-\mathrm{ArN}_2-]_l-[-\mathrm{Ar}-]_m-[-\mathrm{ArS}-]_n-$$

However, this reaction can take place also by a mechanism of nucleophilic substitution[73, 74]. In the homopolycondensation of *p*-mercaptobenzenediazonium chloride in aqueous solution at pH 7, for example, an insoluble solid product is obtained, whose colour is apparently due to the presence of azo-groups in the polymer chain[74]. The overall equation for the reaction can be written

$$2n\overset{+}{\mathrm{H}}\overline{\mathrm{S}}\mathrm{C}_6\mathrm{H}_4\overset{+}{\mathrm{N}}_2\overset{-}{\mathrm{Cl}} \rightarrow -[-\mathrm{S}-\mathrm{C}_6\mathrm{H}_4-\mathrm{S}-\mathrm{N}{=}\mathrm{NC}_6\mathrm{H}_4-]_n- + nN_2 + n\mathrm{HCl}$$

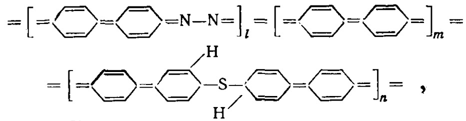
with growth of the polymer chain due to interaction of the zwitterions

$$2\overline{S}C_6H_4N_2^+ \rightarrow -S-C_6H_4SC_6H_4N_2^+ + N_2 .$$

The infrared spectra of the product contain absorption bands due to diazo-sulphide groups, as well as *para*- and *meta*-disubstituted and 1,2,4-trisubstituted benzene rings, which may be centres of chain branching and cross-linking. Even after heat-treatment 150–200°C, with evolution of nitrogen and predominant formation of poly-(*p*-phenylene sulphide) structures, nitrogen could not be completely eliminated from the polymer.

4. Polycondensation of *p*-Halogenobenzenethiolates

The homopolycondensation of metal salts of *para*-halogenated thiophenols is now one of the most promising and quite widely investigated methods for obtaining poly(arylene sulphides). This reaction was first described in 1960 by Lenz et al.[15], and can be represented by the general scheme

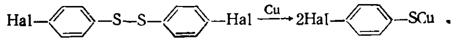


Various copper salts and amines can be used as catalysts, in amounts from 0.01 mole % to equimolecular relative to the initial thiolate[75, 76].

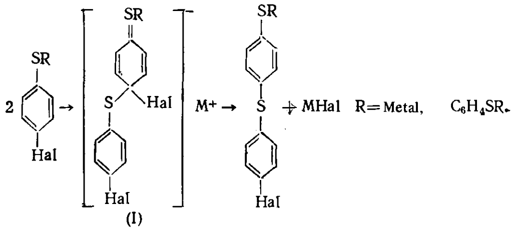
Good yields of poly(arylene sulphides) having high reduced viscosities are obtained by the homopolycondensation of *para*-halogenated thiols in the presence of catalytic quantities of dihalogenobenzenes[77]. Either soluble or infusible and insoluble polymers are obtained depending on the conditions. If the *para*-halogenated thiolate undergoes polycondensation in the mass at temperatures 10–20 deg below the melting point of the initial thiolate, for example, linear polymers are obtained; at higher temperatures infusible and insoluble products are formed under these conditions.

The rate of polycondensation in solution exceeds that in the solid state[78] by factors of 50–100. Depending on the organic solvent used—pyridine, quinoline, dimethylformamide, dimethyl sulphoxide—the process can be carried out over a wide temperature range[75]. Poly(arylene sulphides) obtained by the polycondensation of *para*-halogenated thiolates in solution had a softening point of 280°C, and according to X-ray diffraction a linear structure.

The initial *p*-halogenobenzenethiolate can be obtained *in situ* by the action of an alkali-metal hydride or carbonate on the thiol[79, 80]. An alternative is the cleavage of dihalogenated aromatic disulphides in the presence of copper powder[81]:



In a suggested[82] mechanism the resonance structure (I) formed in the first stage is responsible for the appearance of an inorganic salt and a dimer (a *p*-halogenophenyl *p'*-mercaptophenyl sulphide), the latter able to undergo further reactions leading to poly-(*p*-arylene sulphides):



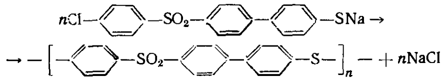
(I)

The activities of halogen atoms in the polycondensation of sodium *p*-halogenobenzenethiolates in pyridine diminish in the sequence I > Br > F ≈ Cl; and those of alkali metals in the polycondensation of a *p*-bromobenzenethiolate diminish in the sequence Li > Na > K.[82] Furthermore, the activities of iodine and bromine are little affected by the change from monomer to polymer, whereas those of chlorine and fluorine as terminal groups of the polymer molecule exceed those in the initial *p*-halogenobenzenethiolate. The nature of the halogen affects also the occurrence of secondary branching and cross-linking reactions, the probability of which decreases in the sequence I > F > Br > Cl. Such reactions disturb the balance of functional groups in the reaction mixture and lower the molecular mass of the resulting polymers. However, when monomers at least 99.6% pure are used, the occurrence of side-reactions is insignificant.

In order to obtain oligo(arylene sulphides) in which the molecular chains terminate only in chlorine atoms copper *p*-chlorobenzenethiolate was subjected to polycondensation in the presence of *p*-dichlorobenzene or di-*p*-chlorophenyl sulphide[76]. Oligomers of analogous structure have been obtained also by the copolycondensation of di-*m*(or *p*)-bromophenyl disulphide and *m*- or *p*-dibromobenzene in the presence of copper powder[83,84]. The molecular mass of the resulting oligomers varies from 186 to 2300 depending on the initial ratio of bisbromophenyl disulphide and dibromobenzene. The polycondensation of *p*-halogenobenzenethiolates in the presence of a monofunctional compound, e.g. bromobenzene or copper benzenethiolate, gives oligo(phenylene sulphides) of low molecular mass containing terminal phenyl groups[85].

Poly(arylene sulphides) containing groups other than sulphide between aromatic rings are obtained by the polycondensation of *p*-halogenobenzenethiolates containing the appropriate group in the initial structure. Thus sodium *p*-*p'*-bromophenoxybenzenethiolate in hexamethylphosphoramide solution gives poly-(*p*-phenoxyphenyl sulphides) (yield reaching 95%) having softening points of 176–188°C and a reduced viscosity of 0.09 (in the above solvent at 30°C)[79].

Linear polymers containing sulphonyl groups in the main chain have been obtained similarly from sodium 4'-*p*-chlorophenylsulphonylbiphenyl-4-thiolate[86,87]:



X-Ray diffraction indicates that the resulting polymer has a high degree of crystallinity, and it softens at ~330°C. The polycondensation of *p*-*p'*-halogenophenylsulphonylbenzenethiol and *p*-halogeno-*p'*-mercaptodiphenyl ketone in dimethylformamide solution at 140°C gives polymers of analogous structure, containing carbonyl and sulphonyl groups between two benzene rings, which are soluble in dimethylformamide, *N*-methylpyrrolidone, and sulphuric acid[88]. The reduced viscosity of their solution in dimethylformamide is 0.3.

The polycondensation of sodium and potassium 4-bromo-2-methylbenzenethiolates and 4-bromo-2,6-dimethylthiolates in dimethylformamide solution yields poly(arylene sulphides) containing methyl groups attached to the polymer chain[75]. The properties of these polymers depend on the structure of the macromolecules. Thus a polymer obtained from sodium 4-bromo-2,6-dimethylbenzenethiolate had molecular mass 740 and softening point 160–180°C, while the corresponding characteristics of poly-(2-methyl-1,4-phenylene sulphide) were 1500 and 60–100°C. The reactivity of the initial *para*-halogenated thiolate diminishes with increase in the number of substituents (methyl groups) in the benzene ring[75].

Perfluorinated poly(phenylene sulphides) have been obtained in high yield by the polycondensation of sodium pentafluorobenzenethiolate in pyridine at 50–200°C.[89-92] Completely halogenated polymers have been obtained also by the polycondensation of pentachloro- and pentabromobenzenethiolates[91,93]. Halogenated poly(phenylene sulphides) are insoluble, dark-coloured powders, which can be used to obtain materials having semiconducting properties.

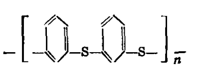
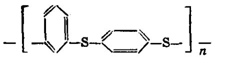
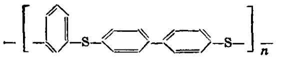
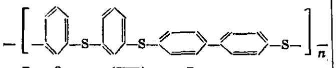
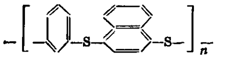
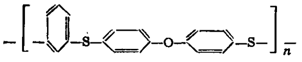
5. Polycondensation of Benzenedithiolates with Dihalogenated Aromatic Compounds

The preparation of poly(arylene sulphides) by the polycondensation of benzenedithiolates with dihalogenated aromatic compounds, which is also of practical interest, was described by Kreuchunas[94] in 1958. When sodium benzene-*p*-dithiolate and di-*p*-chlorophenyl sulphone were boiled in ethanolic solution for 4 h, poly(arylene sulphides) of not very high molecular mass were obtained.

It was proposed[95,96] that the molecular mass could be increased by carrying out the polycondensation in polar organic solvents of high boiling point, e.g. dimethyl sulphoxide, dimethylformamide, dimethylacetamide, etc., and by using dihalogenated aromatic compounds in which the halogen atoms were activated by bivalent electron-deficient groups located between aromatic rings containing halogen in the *para* position, and also by univalent electron-accepting groups present in the dihalogenobenzene as substituents. The poly(arylene sulphides) obtained in this way had specific viscosity 0.32 (in *N*-methylpyrrolidone at 20°C).

The viscosity of the poly(phenylene sulphides) obtained from benzene-*m*-dithiol and *p*-dibromobenzene in dimethylformamide in the presence of potassium carbonate initially increases[80] on polycondensation, after which it falls as the duration of the process lengthens to 96 h.

Table 4. Dependence of properties of poly(arylene sulphides) on structure of monomer unit.

Polymer	Dihalogenoarene	Softening temp., °C	Viscosity, dl g^{-1}*
	*m*-dibromobenzene	100—120	0.1
	*p*-dibromobenzene	110—140	0.15
	4,4'-dibromobiphenyl	160—190	—
	*m*-dibromobenzene + 4,4'-dibromobiphenyl (1 : 1)	85—100	0.11
	1,4-dibromonaphthalene	155—195	—
	di-*p*-bromophenyl ether	55—70	0.07

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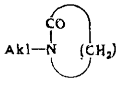
* Viscosities determined for a 0.5% solution in hexamethylphosphoramide at 30°C.

Table 4 lists properties of various poly(arylene sulphides) obtained by polycondensation of benzene-*m*-dithiol with dibrominated aromatic compounds in dimethylformamide[80]. The softening points obviously depend on the structure of the macromolecules: introduction of an oxygen atom into the main chain lowers the softening temperature considerably, but biphenylylene units raise it.

However, optimum production of fibre-forming poly(arylene sulphides) of high molecular weight is achieved by the polycondensation of 25–40 wt.% of dithiolates and bis-*p*-chlorophenyl sulphone in *N*-methylpyrrolidone at 140–160°C for 4–5 h.[97,98] Dihalogenated aromatic compounds in which the halogen atoms are inactive can also be used, e.g. *p*-dichloro- or *p*-dibromo-benzene[99], but a catalyst is then necessary—a copper compound, e.g. cupric oxide, copper acetate, a halide, etc., or *N*-bromosuccinimide (0.06–3 wt.%)—and temperatures of 200–210°C are required. In order to diminish the quantity of byproducts, whose formation is due to the high-temperature (above 140°C) decomposition and oxidation of *N*-methylpyrrolidone, cyclic lactams of general formula



$m = 5-11$,

e.g. *N*-methylcaprolactam, have also been used[100].

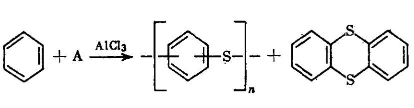
Aromatic dithiolates are usually prepared directly in the apparatus for their polycondensation with dihalogenated aromatic compounds. For this purpose the dithiol is treated with aqueous alkali[99,101], or an alkali-metal carbonate is gradually added to a solution of the dithiol in dimethylformamide[80,96,102]. The hydrogen halide evolved is removed by means of ammonia, diethylamine, morpholine, etc. introduced directly into the reaction space. This increases the rate of polycondensation and yields poly(arylene sulphides) of higher molecular mass[100].

Poly(arylene sulphides) containing functional groups have also been obtained from dithiolates and polyhalogenated aromatic compounds. Thus the reactions of aromatic dithiols with perchlorinated aromatic compounds in the presence of bases gives fusible and soluble poly(arylene sulphides) containing perchlorinated aromatic groups in the main chain[103,104]. After pressure moulding at 400°C such polymers lose their solubility in benzene.

The copolycondensation of benzene-*m*-dithiol with *p*-dibromobenzene and 2,4- or 3,5-dichlorobenzonitrile yields poly(phenylene sulphides) containing nitrile groups[80,105,106], but the action of excess of the dithiol on the dibromobenzene gives polymers having terminal mercapto-groups, treatment of which with *p*-bromobenzonitrile in dimethylformamide containing potassium carbonate gives poly(phenylene sulphides) with terminal nitrile groups. Polymers containing in the main chain sulphur, oxygen, and also various other groupings between the benzene rings are obtained by the copolycondensation of aromatic dithiols with a mixture of two dihalogenated aromatic compounds[107]. Analogous copolymers have been obtained also by using a mixture of aromatic dithiol and diol with the dihalogenated compounds[108]. Another alternative is the polycondensation of *p*-mercaptophenol with the dihalide[100,109].

6. Reaction of Aromatic Compounds and their Derivatives with Sulphur or its Chlorides

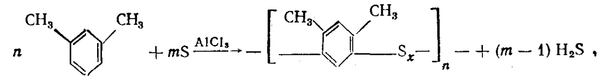
The reaction of benzene with sulphur when heated in the presence of aluminium chloride was first effected in 1888 by Friedel and Crafts[110], when relatively simple compounds—hydrogen sulphide, benzenethiol, diphenyl sulphide and disulphide, thianthren, isothianthren, etc.—were isolated. It was shown somewhat later[111,112] that under these conditions an amorphous polymer having a softening point of ~295°C can be obtained in yields up to 80%. Elementary analysis indicates that the monomer unit in the polymer is C_6H_4S, so that formation of the poly(phenylene sulphide) can be represented by the general scheme[113]



A = S, S_2Cl_2, SCl_2 ,

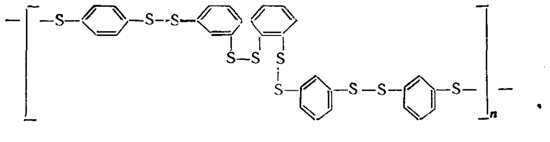
The quantity of byproducts formed—thianthren and diphenyl sulphide—depends on the initial content of aluminium chloride, increase in which increases formation of the sulphide and diminishes that of thianthren[114]. Complexes of aluminium chloride with these two compounds were also isolated[115]. The reaction between aromatic hydrocarbons and sulphur has therefore been carried out[116] in the presence of sulphuric acid under increased pressure at 220–300°C. Poly(arylene sulphides) obtained in this way from benzene, naphthalene, and anthracene softened at ~100°C. Since their sulphur content varied from 10% to 90%, it was supposed[115] that the sulphidation of aromatic rings under these conditions yields polymers containing polysulphide groups $[ArS_x]_n$.

Benzene derivatives can also be used for reaction with sulphur. Thus resinous products useful for medicinal purposes were obtained from xylene and sulphur in the presence of aluminium chloride at 80–90°C.[117] It has since been established[118] that under these conditions only *m*-xylene forms polymeric products, probably by the mechanism



The formation of polymers having a regular structure is attributed[118] to the influence of substituents in the benzene ring. With increase in the content of sulphur or the concentration of aluminium chloride in the initial mixture the quantity of combined sulphur in the polymeric product increases to a limiting maximum of 11.1%. Polymers containing >8% of sulphur solids of molecular mass 1000 and softening point 40°C. Later investigation has shown[119] that the aromatic rings in the polymer from *m*-xylene are interlinked mainly by disulphide groups.

Gaseous hydrogen chloride is evolved from the action of sulphur on chlorinated benzenes (e.g. chlorobenzene or dichlorobenzenes) at 225–350°C (and also at high pressures)[120]. The solid products are oligo(phenylene sulphides) containing 40–80 wt.% of sulphur, softening at ~100°C, and soluble in carbon disulphide. When they are decomposed by metallic sodium in liquid ammonia[121], a mixture of isomeric dithiolobenzenes is isolated in 35% yield, comprising 50% of the *para* isomer with 25% each of the *ortho* and *meta* isomers. It is thus confirmed[121] that the oligomers contain all three types of substituted aromatic rings interlinked by disulphide groups:



Black sulphur-containing polymers with improved electrical conductivity and electron-exchange properties, infusible and insoluble in organic solvents, have been obtained by the polycondensation of sulphur with chloranil, 1,4-naphthaquinone, anthraquinone, or 1,5-dihydroxyanthraquinone in the molecular proportions 4–12:1 at 280–400°C.[122] The polymer chains contain not only monosulphide-linked quinoid but also thianthren groups, and may be joined by polysulphide cross-links. Excess of sulphur increases the likelihood of polysulphide bonds.

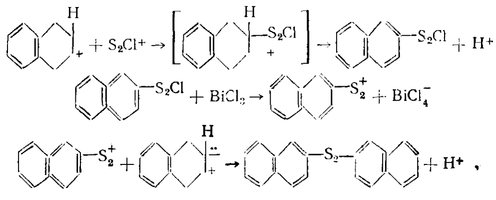
The structure of the products formed from aromatic hydrocarbons with sulphur and especially sulphur chlorides is significantly influenced by the nature of the catalyst. The reaction of benzene with sulphur dichloride in the presence of aluminium chloride yields thianthren as main product[123]. In the presence of sulphuric acid, however, sulphur dichloride acts on benzene, toluene, or xylene to give polymeric products as powders readily soluble in xylene[124].

The action of sulphur chlorides on diphenyl ether and sulphide in the presence of aluminium or its salts yields cyclic compounds—phenoxatin and thianthren respectively[125,126]—intramolecular cyclisation probably being due to formation of complexes of aluminium or its salts with the initial heteroatomic products, containing oxygen and sulphur respectively. In order to obtain linear compounds of high molecular weight the reaction between diphenyl ether and sulphur chloride has been conducted in the presence of iron powder or anhydrous iron(III) chloride in chloroform solution at room temperature[125-127]. The resulting polymers (obtained in quantitative yield) had a reduced viscosity of 0.1 (in 1% solution in hexamethylphosphoramide) and a softened point at 147–156°C. Elementary analysis, X-ray diffraction, and n.m.r. spectra indicated that polymers formed from diphenyl ether and sulphur dichloride are crystalline and contain only monosulphide links between aromatic rings, whereas those obtained from the ether and sulphur monochloride are amorphous and contain not only monosulphide but also up to 15% of disulphide groups. However, it has been reported[128] that polymers obtained from diphenyl sulphide and sulphur dichloride, partly soluble solids softening at 125°C, also contain up to 10% of disulphide groups.

Poly(arylene sulphides) of diverse structure and molecular mass up to 2000 have also been obtained[129] by the polycondensation of aromatic hydrocarbons with sulphur chlorides in chloroform solution in the presence of various metals (bismuth, tin, or antimony) at ~60°C. Chlorides of the metals are probably formed in the first stage, and the overall reaction of naphthalene with sulphur dichloride in the presence of bismuth can be written

$$3S_2Cl_2 + 2Bi \rightarrow 2BiCl_3 + 3S_2$$

$$BiCl_3 + S_2Cl_2 \rightarrow [BiCl_3 \cdot S_2Cl_2] \rightarrow BiCl_4^- + S_2Cl^+$$



Further growth of the polymer molecule probably involves di-2-naphthyl disulphide formed from chlorodisulphanyl ions, polarised naphthalene, and bismuth chloride, which appear as intermediate products. However, infrared spectral data, elementary analysis, measurements of molecular mass, and the separation of elementary sulphur on prolonged storage indicate that the products are oligomers, whose molecules comprise seven or eight ββ'-disubstituted naphthalene groups, interlinked not only by disulphide but also by polysulphide bonds. The formation of such groups can be explained by the participation in intermediate reactions of polysulphur chlorides resulting from decomposition of sulphur monochloride:

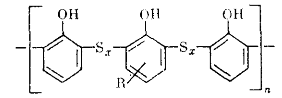
$$2S_2Cl_2 \rightarrow SCl_2 + S_3Cl_2$$

$$2S_nCl_2 \rightarrow S_{n-1}Cl_2 + S_{n+1}Cl_2\ .$$

Oligomers obtained from anthracene or phenanthrene under the same conditions contain respectively ββ'-substituted anthracene or 2,3- and 6,7-substituted phenanthrene groups, as well as di- and poly-sulphide groups. The yield of oligomers is 49–63% depending on the nature of the catalyst[129].

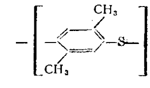
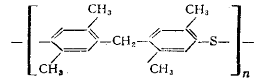
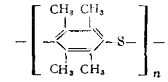
Poly(arylene sulphides) of molecular mass up to 3×10^6 are obtained[130] by reaction between various aromatic compounds and sulphur halides at a constant pH in the presence of up to 35% of an activator (an alkali or a carboxylic acid or ester). The polymer thus obtained from anthracene and sulphur chloride is a powder having a softening point of ~90°C.

Poly-(2-hydroxy-1,3-phenylene polysulphides) of general formula



where R = Alk and $x = 1-7$, are synthesised by the polycondensation of *p*-alkylphenols or their substituted derivatives with sulphur monochloride or dichloride[131,132], or of phenolic compounds with sulphur in the presence of a basic catalyst (e.g. sodium hydroxide) at 120–200°C.[133]

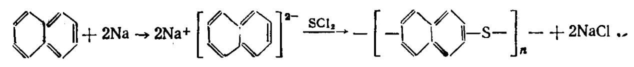
Table 5. Properties of methylated poly(arylene sulphides).

Arene	Monomer unit	Yield, %	Softening temp., °C	Mol. wt.	Cl, %
p-Xylene		60	270—285	1500	7.75
2,2',5,5'-Tetramethyl diphenylmethane		55	240—250	1300	11.88
1,2,4,5-Tetramethylbenzene		70	291	950	6.5

Methylated poly(arylene sulphides) have been obtained by the action of sulphur dichloride on methylated aromatic compounds in the presence of iron powder[128]. Table 5 gives several characteristics of such polymers. The products had a regular structure and contained up to almost 12% of chlorine. An interesting feature of this reaction is that, whereas *p*-xylene and sulphur dichloride gave methylated poly(phenylene sulphides) under these conditions, the polycondensation of *p*-xylene with sulphur in the presence of aluminium chloride does not yield polymeric products[118]. Oil-soluble chlorinated poly(phenylene sulphides) are obtained by the polycondensation of tri-, tetra-, and penta-chlorobenzenes with sulphur monochloride in the presence of aluminium chloride[134,135].

Such polymers soften above 85°C, the viscosity of the melt is 0.256 P (at 131°C), and they contain up to 50% of chlorine.

Furthermore, a process has been elaborated[136] for the preparation of poly(arylene sulphides) in high yields by the reaction of dipotassium diphenylbutane, disodium diphenylmethane, disodium naphthalene, and other dimetallated aromatic derivatives with sulphur halides in inert solvents (oxolan, n-hexane, etc.) at temperatures from −75 to +75°C. The reaction of disodium naphthalene with sulphur dichloride can be represented in general as

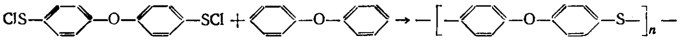


The products have softening points of ~175°C, and can be used as thermostable adhesives.

An examination of thermodynamic aspects of the formation of sulphur polymers by heating has shown[137] that polymeric phenylene polysulphides can be obtained from chlorinated aromatic compounds and polymeric sulphur.

7. Homopolycondensation of Aromatic Sulphenyl Chlorides and their Copolycondensation with Aromatic Hydrocarbons or Thiols

The first descriptions have appeared[138–140] of the preparation of poly-(*p*-phenoxyphenylene sulphides) by the copolycondensation of diphenyl and di-*p*-chlorothiophenyl ethers in the presence of metal powders or salts in an inert atmosphere away from the light at room temperature:



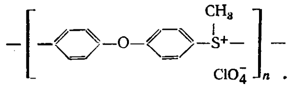
The resulting polymers dissolve readily in aromatic hydrocarbons and polar organic solvents. Table 6 gives data on the influence of the nature of the catalyst on the yield and certain properties of the products. Elementary analysis and n.m.r. spectra indicate that the polymer molecule contains *para*-substituted aromatic rings joined together by mono- and di-sulphide groups, the latter amounting to 9–10%. The formation of disulphide links is attributed[138–140] to reaction between the sulphenyl chloride groups, which is supported by the evolution of gaseous chlorine. The mechanism of polycondensation has been studied also on model compounds.

Table 6. Dependence of properties of polymers on nature of catalyst.

Catalyst	Yield, %	Softening temp., °C	Viscosity, dl g⁻¹*
Fe	75	160—170	0.12
$FeCl_3$	75	156—189	0.10
$SnCl_4$	68	153—173	0.07
$AlCl_3$	38	140—175	0.08

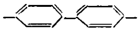
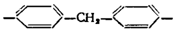
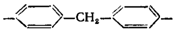
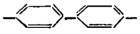
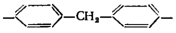
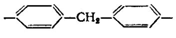
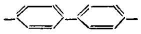
* Viscosities determined for 1% solutions in hexamethylphosphoramide at 30°C.

Polymers containing aromatic rings linked by sulphide groups are obtained[140] by the homopolycondensation of benzenesulphenyl and *p*-phenoxybenzenesulphenyl chlorides in chloroform solution in the presence of metal powders or Lewis acids. The poly-(*p*-phenoxyphenylene sulphide) was obtained in 53% yield and softened at 134–145°C. Poly(alkyl- and aryl-*p*-phenoxyphenylsulphonium) salts, with decomposition points of 165–275°C and reduced viscositities of 0.06–0.55, have been obtained[141] by the homopolycondensation of alkyl and aryl *p*-phenoxyphenyl sulphides in a mixture of 70% of perchloric acid and phosphoryl chloride in argon at 25°C for 20 h followed by heating at 50–60°C. The structure of the polymer obtained from the methyl sulphide corresponds to the formula



Such a polymer is soluble in formic acid and in aprotic polar solvents. On dealkylation by boiling in pyridine it is converted into a poly(*p*-phenoxyphenylene sulphide) of softening point ~188°C and reduced viscosity 0.27.

Table 7. Dependence of properties of polymers on structure of initial monomers.

R	R′	Molecular mass*	Sulphur, %	
			expt.	calc.
		(insol.)	29.3	29.6
		(2–4) x 10³	27,6	27.8
		(insol.)	28.5	28.7
		(2–4) x 10³	31.2	34.6
		(insol.)	35.1	36.0

*Determined by osmometry.

Poly(arylene sulphides) have been obtained in yields up to 90% also by the polycondensation of aromatic disulphenyl chlorides with aromatic dithiols in oxolan solution at 20°C:[142]

$$n\text{ClS—R—SCl} + n\text{HS—R}'\text{—SH} \xrightarrow[-\text{HCl}]{} \text{— [—S—R—S—S—R}'\text{—S—]}_n \text{ —} ,$$

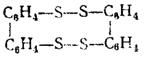
Table 7 shows that poly(arylene disulphides) containing biphenylylene groups are insoluble in the usual organic solvents, in contrast to those containing *m*-phenylene or diphenylmethane groups, and are readily soluble in oxolan and chloroform. The structure of the polymeric disulphides has been confirmed by infrared and n.m.r. spectra and by X-ray diffraction[143]. Redistribution of monomer units by interaction of the disulphide bond with the chlorothio-group does not take place, and the polymers have a regular structure.

8. Preparation of Poly(arylene Disulphides) by the Oxidation of Dithiols

In 1909 Zincke and Frohnberg[144] oxidised benzene-*p*-dithiol with various oxidants (e.g. air, iron chlorides, peroxides, sulphuric and nitric acids) in acetic acid, and isolated as main product an amorphous yellow powder, insoluble in the usual organic solvents. Analysis suggested a polymer having the monomer unit $[C_6H_4.S_2]_n$. Treatment with copper powder and heating in order to cleave the disulphide bonds gave an oil, from which a cyclic dimer, *pp'*-diphenylene bisdisulphide, was obtained[145]. When benzene-*p*-dithiol was oxidised with chlorine or bromine under the same conditions, the precipitated product passed after some time back into solution, from which benzene-*p*-disulphonyl chloride or bromide respectively was then isolated[144].

However, the oxidation of benzene-*p*-dithiol with ethanolic iodine gives an approximately 75% yield of a solid product that is partly soluble in organic solvents and softens at 198–202°C.[128] Elementary analysis (sulphur content 46.12%) and X-ray diffraction indicate that it is a linear poly-(*p*-phenylene disulphide).

Biphenyl-4,4'-diol is oxidised more slowly by air than by alkaline solutions[146], to give a cyclic tetraphenylene tetrasulphide



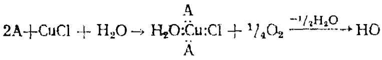
$$\begin{array}{ccc} C_6H_4\text{—}S\text{—}S\text{—}C_6H_4 \\ | \qquad\qquad\qquad | \\ C_6H_4\text{—}S\text{—}S\text{—}C_6H_4 \end{array}$$

as an insoluble amorphous product.

Aliphatic sulphoxides have also been used as oxidants. The oxidation of dithiols when solutions in dimethyl sulphoxide are heated at 95–170°C can be represented by the general scheme[147]

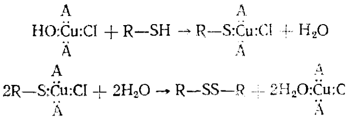
$$n\text{HS—R—SH} + nR'_2SO \rightarrow \text{H—}[\text{—S—R—S—}]_n\text{—H} + nH_2O + nR'_2S \ .$$

More detailed investigation of the action of various oxidants on aromatic dithiols has established[148] that iodine and hydrogen peroxide tend to increase not only the rate of formation but also the yield of poly(arylene disulphides), while the use of catalysts (e.g. a mixture of a copper salt and an amine, acid, or alkali) dissolved in an inorganic solvent (e.g. water) at temperatures of 0 to 38°C promotes the formation of poly(arylene disulphides) of higher molecular mass. An intermediate complex is probably formed in the inorganic solvent, according to the general scheme (for a mixture of copper(I) chloride and an amine A)



$$2A + CuCl + H_2O \rightarrow H_2O{:}\overset{A}{\underset{A}{\ddot{C}u}}{:}Cl + {}^1/_4O_2 \xrightarrow{-{}^1/_2H_2O} HO{:}\overset{A}{\underset{A}{\ddot{C}u}}{:}Cl \ .$$

Its reaction with a mercapto-group can then be written



$$HO{:}\overset{A}{\underset{A}{\ddot{C}u}}{:}Cl + R\text{—}SH \rightarrow R\text{—}S{:}\overset{A}{\underset{A}{\ddot{C}u}}{:}Cl + H_2O$$

$$2R\text{—}S{:}\overset{A}{\underset{A}{\ddot{C}u}}{:}Cl + 2H_2O \rightarrow R\text{—}SS\text{—}R + 2H_2O{:}\overset{A}{\underset{A}{\ddot{C}u}}{:}Cl \ ,$$

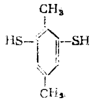
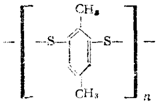
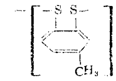
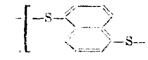
This reaction results in regeneration of the amine complex of the copper salt and formation of organic disulphides. It is noteworthy that the polycondensation of dithiols also occurs in conformity with the mechanism suggested for the oxidation of thiols.

Table 8 gives the structural formulae of the initial dithiols subjected to oxidation together with characteristics of the poly(arylene disulphides) obtained in quantitative yield. The polymer from 4-methylbenzene-1,2-dithiol dissolves readily in chloroform, whereas that from naphthalene-1,5-dithiol is insoluble in the usual organic solvents.

9. Polytransarylation of Aromatic Sulphides

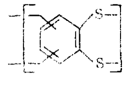
A process suggested comparatively recently[149] for obtaining poly(arylene sulphides) by the polycondensation of aromatic sulphides is to heat them in the presence of Friedel–Crafts catalysts to 160–350°C. Either insoluble or solvent-soluble products can be obtained depending on the conditions. Thus when diphenyl sulphide is heated with 6 mole % of aluminium chloride at 200°C for 4 h, benzene distils off and an 85.2% yield is obtained of a powder containing 85.6% of a benzene-soluble product of molecular mass 450 (determined cryoscopically in benzene) and softening temperature 110–120°C. Elementary analysis indicates a 37.53% sulphur content, exceeding by 8% the content for the monomer unit $[C_6H_4.S]_n$. Furthermore, preparative thin-layer chromatography has revealed thianthren among the reaction products[150].

Table 8. Structure of polymers obtained from initial dithiols.

Dithiol	Monomer unit	Softening point, °C
		~190
		~118
		>250

From the results it is considered[150] that the mechanism of the polycondensation of diphenyl sulphide is analogous to that of the well known transarylation of diarylalkanes[151] and that polycondensation is accompanied by formation of an intermediate complex of diphenyl sulphide with aluminium chloride. The appearance of cyclic products is attributed to the greater activity of the *ortho* position in the aromatic ring relative to the sulphur substituent. Cyclic compounds containing *ortho* substituents had been isolated earlier in the transarylation of diarylalkanes[152].

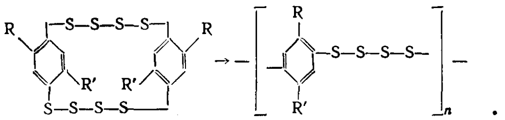
Since products of the transarylation of diphenyl sulphide contain neither thiol nor disulphide groups according to the infrared spectra and chemical analysis, the structure of the oligomers may contain predominantly polythianthren groupings.



The presence of such structures among the reaction products is confirmed by mass spectrometry and also by the polymerlike conversion of these products into the corresponding sulphones followed by analysis of thermal decomposition products of the polymer analogues.

10. Polymerisation of Cyclic Sulphides

Poly(arylene tetrasulphides) have been obtained by the thermal polymerisation of cyclic diarylene bistetrasulphides in the mass or in solution in a stream of an inert gas at 150–220°C:[153-155]



R=R'=OC_2H_5 (I); R=R'=OCH_3 (II); R=OCH_3, R'=Cl (III).

Table 9 gives conditions of preparation, reduced viscosity, and molecular mass for a few poly(arylene tetrasulphides). The products are stable under normal conditions and possess satisfactory adhesion to metals.

Table 9. Reaction conditions and properties of poly(arylene tetrasulphides).

Monomer	Conditions	Reduced viscosity, 0.4 g/100 ml $CHCl_3$	Mol. wt. (number-av.)
(I)	in mass, 195°C, 1 h	0.21	15 781
(I)	in bromobenzene, 150°C, 3 days	0.08	7 129
(I)	in bromobenzene, 150°C, 16 h	0.06	4 653
(II)	in mass, 220°C, 1 h	0.08	—
(III)	in mass, 195°C, 1 h	0.04	—

11. Polycondensation of Dihalogenated Aromatic Compounds with Alkali Metals

Application of the Wurtz–Fittig reaction to di-*o*(and *p*)-chlorophenyl sulphides with metallic sodium has recently[156] yielded soluble poly-(*o*(and *p*)-diphenyl sulphides), respectively plastic at room temperature and solids passing into a state of viscous flow at 170–200°C.

III. PRACTICAL APPLICATIONS

A previous review[3] has examined in sufficient detail the properties of various poly(arylene sulphides), the changes undergone under processing conditions, and the properties of articles made from them. Below, therefore, we give only general information on properties and practical applications, noting primarily the main lines of development in the light of recent work.

Poly(arylene sulphides) are distinguished by high thermal[8,92,95,157-163], thermo-oxidative[15,113,157-159,164,165] and chemical[17,157,162,166-168] stability, fire resistance[157,166,187-192], non-toxicity[24,183,193,194], and several other specific properties[24,103,164,195-201]. They can be readily oxidised by various oxidants (hydrogen peroxide[95-97,162,202-206], nitric acid[207], etc.) to poly(arylene sulphoxides or sulphones), a process that should be applied to the ready-made materials and articles[208]. Heat-treatment has been used to diminish the fluidity and raise the softening point[184,192,209-214]: thus heating at 320°C for 300 h raised the working range of a poly(arylene sulphide) to higher temperatures (from 100 to 200°C and above)[211]. The maximum operating temperature at which films retain their strength for a long time (>10 weeks) has been regarded[157,158,164,166,187,214] as 260°C, but the temperature of prolonged operation of the polymer has been restricted[188] to 180°C.

Poly(arylene sulphides) surpass polysulphones and polyimides in many physicochemical indices[164]. They are used as adhesives for glass-fibre laminates[164,166,180,182,215-223], which have better mechanical strength at 204°C than has polyethylene at room temperature[166].

Poly(arylene sulphides) provide good electrically insulating materials[187-189,224-228]. Thus the dielectric constant of poly(phenylene sulphide) has been given as 3.1 (10^6 Hz), the dielectric loss angle as 0.0007 (10^6 Hz), the dielectric strength as 23.8 kV mm^{-1}, and the bulk resistance as 10^{16} ohms cm.[157,166]

Great attention has been paid to studying the properties of films based on poly(phenylene sulphides)[7,157,162,164,166,168,171,172,184,187-189,229-244], which show good adhesion to various supports[24,82,164,195-199].

Compositions of poly(arylene sulphides) with various fillers can be processed into articles by injection moulding, extrusion, pressure moulding, etc.[214,215,223,229,245-251]. Articles made of such compositions can be ground, milled, drilled, welded ultrasonically, metallised with chromium and other metals, and also threaded[252]. This explains the widespread use of poly(arylene sulphides) and articles made from them in mechanical and electrical engineering, aircraft construction, chemical industry, and other technologies.

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Application of Photoelectron Spectroscopy in the Study of Catalysis and Adsorption

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Problems associated with the application of photoelectron spectroscopy (PES) in the study of catalysis and adsorption are examined, the physical principles of PES and the experimental technique are briefly described, and an account is given of the results of the application of the method to the study of metallic, alloy, oxide, deposited, and zeolite catalysts. It is shown that the method can be used successfully to investigate the valence and physical states and the surface concentrations of elements in catalysts, the nature of the adsorption complexes, and the mechanism of surface reactions.
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I. INTRODUCTION

Since the 1970s, X-ray photoelectron spectroscopy (XPES) has been widely used in chemical research. The method is based on the phenomenon of the photo-electric effect. The energy distribution of the inner and valence electrons of the test substance is analysed in the spectra excited by monochromatic X-rays. The practical application of the method became possible when a group of Swedish workers headed by Siegbahn developed in the middle 1950s apparatus which made possible the analysis of photoelectrons with a high resolution and sensitivity. Their studies showed that XPES is extremely sensitive to changes in the electronic structures of substances which occur on chemical reaction[1,2]. During the same years, Vilesov et al.[3] developed the practical principles of the application of ultraviolet photoelectron spectroscopy (UPES) in the study of gases. At the present time both these methods have been constructively combined and are used successfully to investigate the gaseous and solid states.

Because of the universality of the information obtained with the aid of XPES, the method has been used to solve various physical and chemical problems. During a short period, more than a thousand studies on complex and organoelemental compounds[4-8] and the electronic structures of solids[8-11] were carried out. Recently a tendency has arisen towards a more vigorous employment of XPES and UPES in the study of surface phenomena: adsorption, catalytic, corrosion, oxidation, etc. processes. In view of a number of its characteristic features, this field of application of the method appears to be the most promising.

1. The photoelectron spectra excited by X-rays record electrons leaving the specimen without loss of energy in non-elastic collisions with lattice elements. Theoretical calculations[12] and numerous experimental studies[13-15] have

shown that the depth of the surface layer from which electrons are emitted for $E_{\mathrm{kin}} \simeq 1000$ eV in most cases does not exceed 20–30 Å. In ultraviolet or synchrotron excitation of the spectra and in the measurement of low-angle photoemission the depth of the analysed layer may be equivalent to several atomic layers[16-18].

2. The energies of the lines and the structure of the spectra of the inner levels characterise the valence state of the elements and the nature of their interaction with the immediate environment; the valence bands characterise the band structure of the solid.

3. The spectra of the inner and valence levels of adsorbates serve as a basis for the determination of the type and geometry of the adsorption bond.

4. The PES method permits a quantitative analysis of the composition of the surface and the adsorption layer.

5. The method is applicable to the study of all the elements in the Periodic System.

There are many reviews devoted to problems of the study of the surfaces of solids[19-27], including heterogeneous catalysts[22-28]. Problems of the study of adsorption on clean surfaces have been repeatedly and most fully discussed[24,27,29-37], but the majority of the reviews have been published abroad and do not deal with studies carried out recently in the USSR. Furthermore, owing to the vigorous development of this field of study, even reviews published in recent years cannot claim to give a complete survey and do not include recently published fundamentally new results, acquaintance with which would promote a rapid adoption of the method in practical catalytic research.

Within the framework of the present review, the authors have considered the results of studies on heterogeneous catalysts, as well as adsorption and catalysis by methods of photoelectron spectroscopy.

II. PHYSICAL PRINCIPLES OF THE METHOD OF PHOTOELECTRON SPECTROSCOPY

Bearing in mind that the physical principles of the PES method and the problems concerned with the interpretation of the spectra have been described in detail in a number of monographs and reviews[1,4,11,22,23,25,30], we shall confine ourselves to a very brief consideration of the main principles of the analysis of the spectra. The binding energy of an electron emitted from a conducting solid is defined by the equation

$$h\nu = E_{\mathrm{kin}} + E_{\mathrm{b}}^{\mathrm{F}} + \varphi_{\mathrm{sp}}, \tag{1}$$

where $h\nu$ is the energy of the quantum (the emission energies of the Al$K\alpha$ and Mg$K\alpha$ lines are 1486.6 and 1254.6 eV and the energies of the He I and He II lines are 21.2 and 40.8 eV respectively), E_{kin} is the experimental kinetic energy of the electrons, $E_{\mathrm{b}}^{\mathrm{F}}$ is the electron binding energy relative to the Fermi level of the material of the spectrometer, and φ_{sp} is the electron work function of the material of the spectrometer. For non-conducting specimens, the determination of E_{b} is complicated for two reasons: (a) an effective electrical contact with the spectrometer is absent; (b) the specimen is charged under the influence of the radiation. (The charging is taken into account using external and internal standards[38-41]; various devices have been suggested to compensate the charge[42,43].)

The determination of the change in E_{b} for the inner levels (chemical shifts) constitutes the main source of information about the change in the valence state of elements, the nature of the chemical bond, coordination, etc. ΔE_{b} is described by the formula[1,5,11,44-46]

$$\Delta E_{\mathrm{b}} = \Delta E(q) + \Delta V + E_{\mathrm{rel.}}, \tag{2}$$

where $\Delta E(q)$ is the change in bond energy caused by the change in the charge of the free ion, ΔV the change in the crystal field potential near the atom investigated, and E_{rel} the relaxation energy of the system caused by the formation of a vacancy at an inner level. The second and third terms of Eqn. (2) in general have the opposite sign to the first term. Allowance for only the first term in Eqn. (2) leads to larger calculated shifts compared with experimental values[1,5,11,44,45]. At the same time there is a correlation between the effective charge on the ion in the compounds and E_{b}.[5,8]

The chemical shift in the spectra of adsorbed molecules is defined by the expression

$$\Delta E = E_{\mathrm{ads}} - E_{\mathrm{gas}} = \Delta E_{\mathrm{b}} + \varphi_{\mathrm{sp}} + \Delta E_{\mathrm{rel}}, \tag{3}$$

where ΔE and ΔE_{rel} are the overall change in the energy of the level and the change in relaxation energy when the molecule passes from the gas phase to the adsorbed state (the "interatomic" relaxation is of decisive importance in chemisorption[46]).

The following method for separating the chemical and relaxation shifts in the spectra of adsorbed molecules has now been adopted. It is suggested that the changes in relaxation energy for non-bonding orbitals, bonding orbitals, and the inner levels are approximately equal. ΔE_{rel} can be determined by studying the physical adsorption of condensation of molecules on inert carriers.

The spectra of the inner levels frequently consist of a set of lines and not singlets, which is due to the multiplet splitting of the inner levels[5,8,47-49], the emission of Auger electrons[1,5,11], and many-electron processes[5,8,48,50-59], arising owing to the instability of the photoionised state of the atom. The mechanism of the formation of satellite lines owing to many-electron processes has not been fully elucidated. Some workers attribute their appearance to the intra-atomic transitions from the valence band to the conduction band[50-53] or to monopole transitions with charge transfer[54-56]. According to other workers, the satellites arise owing to the interaction of the emitted and outer unpaired electrons, leading to the inversion of the spin of the latter[57,58]. The parameters of the satellite structure change when the valence state[54-56], the spin density[57,58], the coordination of the atom[54-56], etc. are altered.

The intensity of the peak in the photoelectron spectrum is described by the formula[1,5,8,60]

$$I_i = FGS_i\sigma_i\lambda_i(E_i)N_i, \tag{4}$$

where F is the intensity of the photo flux, G the fraction of the overall electron flux measured by the spectrometer (it depends on the geometry of the specimen), S_i the sensitivity of the analyser and the detector, σ_i the atomic photoionisation cross-section of the ith level, $\lambda_i(E_i)$ the average path traversed by electrons (with $E_{\mathrm{kin}} = E_i$) without undergoing non-elastic collisions in the specimen, and N_i the number of electrons emitted from the ith level of the element investigated. In practice, when the concentrations of elements are determined, one measures the relative intensities[1,5,8,12,61-64]. For two elements, the intensity ratio can be expressed thus:

$$I_1/I_2 = T_{1,2}\frac{\sigma_1}{\sigma_2}\frac{N_1}{N_2}, \qquad T_{1,2} = \frac{S_1(E_1)\cdot\lambda_1(E_1)}{S_2(E_2)\cdot\lambda_2(E_2)}. \tag{5}$$

There are now fairly reliable calculated and experimental data for σ_i[61-64] and λ_i[13-15,36,60]; the problem of the quantitative analysis of "thick" homogeneous specimens is therefore solved successfully. However, analysis of heterogeneous systems requires allowance for many additional factors (see Section III).

Studies on the angular distribution of photoelectrons[16, 17, 32, 33, 65, 66], which it is hoped will increase the surface sensitivity of PES and will make possible the investigation of the geometry of adsorption bonds, have begun recently.

Table 1 presents certain parameters of standard and modernised commercial spectrometers, which illustrate the technical scope of the PES method[87]. Certain types of unique laboratory apparatus have additional possibilities: additional monochromatisation of the X-rays makes it possible to obtain the line width (~ 0.2 eV)[68]; the employment of a synchrotron as the source of radiation makes it possible to alter continuously the energy of the quanta from 5 to 450 eV and to investigate systematically the dependence of the intensity on $h\nu$.[18] Table 1 shows that the analytical possibilities of XPES are small; however, when surfaces are investigated, this method is irreplacable. The employment of combined apparatus, involving several methods (UEPS–AES–LEED, XPES–APES–UPES, and UPES–SIMS–LEED†) has incontrovertible advantages in combined studies of surfaces, but the intrinsic possibilities of each method are then restricted.

Table 1. Parameters of electronic spectrometers*.

Name of firm and instrument	Limiting resolution on X-ray excitation, eV	Sources of excitation of spectra	Limiting sensitivity w.r.t. Au(4*f*) line, counts s^{-1}	Limiting vacuum, mmHg	Devices for treatment of specimens
Hewlett-Packard, HP 5950 A	0.5	AlK_α, MgK_α, AlK_α monochr.	10^5	10^{-8}	treatment camera, ion gun,
Vacuum Generators, ESCA-3 MK II	0.9	AlK_α, MgK_α, He I, He II, electron flux·	10^5	5.10^{-11}	ditto
A. E. I. ES-300	0.5	AlK_α, MgK_α, He I, He II AlK_α monochr. electron flux	10^5	10^{-10}	»
Physical Electronics, SAM/ESCA-549	0.9	AlK_α, MgK_α	—	10^{-10}	»
McPherson, ESCA-36	0.9	ditto	—	10^{-10}	»

*The average sensitivity with respect to elements is 0.1–1.0 wt.%; the minimum amount of adsorbate on the surface is 0.05–0.1 of a monolayer.

The method of preparation of the catalyst specimens and their treatment and the procedures used in the measurement of the spectra have been examined in a number of reviews[23, 25, 26]. One should note that the most effective elimination of impurities from the surface and dehydration are achieved when the catalysts are treated *in situ*. After the reaction the catalyst studied must be transferred to the spectrometer without any external influences on the specimen. Unfortunately these self-evident requirements were not fulfilled in all experimental studies.

III. RESULTS OF THE STUDY OF CATALYSIS AND ADSORPTION BY PHOTOELECTRON SPECTROSCOPY

1. Metals and Alloys

It has been shown[9-11, 69-79] that the stretching vibration band spectra reproduce fairly effectively the principal characteristics of the distribution of the density of the states of valence electrons in metals and alloys. Studies on many transition (Mn, Fe, Co, Ni, Cu) and noble (Ag, Pd, Au, Rh, Ir, and Pt) metals and their alloys[11, 69, 72] led to the conclusion that the d-states of both components in non-ordered binary alloys to a large extent retain the localisation characteristic of the pure metal; when an alloy is formed, the inner levels of the metals undergo only a slight perturbation[11]. Studies have been made recently to investigate the band structure of metals and alloys, using monochromatised sources of X-rays and UPE spectroscopy[11, 76, 77, 79].

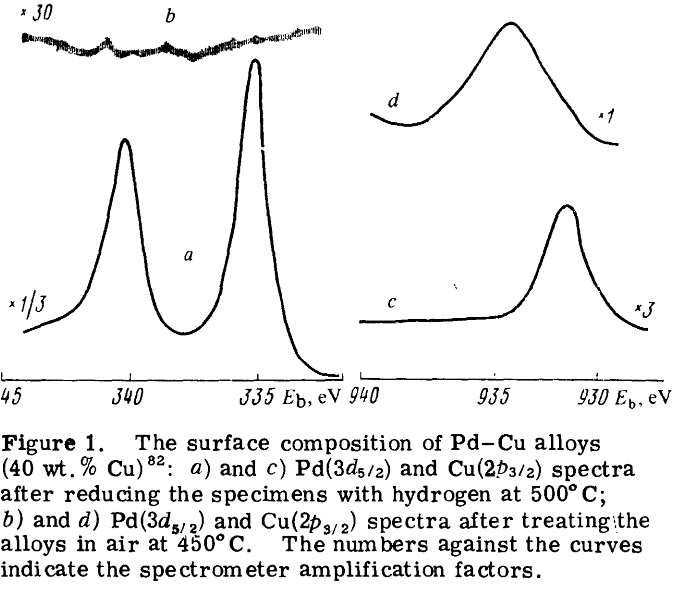

Figure 1. The surface composition of Pd–Cu alloys (40 wt.% Cu)[82]: *a*) and *c*) Pd($3d_{5/2}$) and Cu($2p_{3/2}$) spectra after reducing the specimens with hydrogen at 500°C; *b*) and *d*) Pd($3d_{5/2}$) and Cu($2p_{3/2}$) spectra after treating the alloys in air at 450°C. The numbers against the curves indicate the spectrometer amplification factors.

The composition of the surface layer of alloys in many instances differs from the bulk-phase composition: on treatment with hydrogen, the surfaces of Pt–Sn, Pt_3–Sn,[80] Ni–Al,[81] and Pd–Al[82] alloys become enriched in the second component. On treatment of the Pd–Cu (40 wt.% Cu) alloy with hydrogen at 400°C, the surface concentration of copper also increases (Fig. 1)[82]. The most marked changes in the surface layer occur in the oxidative regeneration of Pd–Cu catalysts. The spectra show that the surface layer is coated by a CuO film whose thickness exceeds 50 Å according to approximate calculations[82]. By employing synchrotron radiation or Auger electron spectroscopy, it is possible to analyse the composition of alloys in depth, starting from a monolayer and continuing up to several tens of atomic layers[80, 83].

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†AES = Auger-electron spectroscopy, LEED = low-energy electron diffraction, and SIMS = secondary ion mass spectrometry.

2. Simple Oxides

Studies devoted to oxides can be divided by convention into three groups: (1) the study of thin oxide films; (2) the study of bulky oxide specimens; (3) the study of two- and multi-component oxide catalysts. Table 2 presents the principal results of studies on oxide films and bulky oxide specimens.

Table 2. Results of the study of oxides by the PES method.

Element	Main results	Changes in spectra; method of determination	References
	Thin oxide films		
Ti	formation of monolayer oxide film observed for exposures to O_2 not less than 7–10 L*	change in the form of valence bands	84
Fe	Fe_3O_4 structure studied	ditto	85
Ni	formation of NiO demonstrated in oxidation of Ni foil	shift in the $Ni(2p_{3/2})$ spectrum	86
Ni	structural differences observed in thin oxide films	position of $3d$ levels of Ni	87
Pt	formation of PtO and higher oxides demonstrated in oxidation of sputtered Pt	shifts in $Pt(4f)$ spectrum	88
Pt, Au	thin films obtained by anodic oxidation investigated	shifts in spectra of $4f$ levels of Pt and Au	89
Mo	formation of F-centres in substoichiometric amorphous MoO_3 films demonstrated; oxygen vacancies found in surface MoO_3 layer	peak near Fermi level; $O(1s)$ peak with E_b = 532.2 eV	90,91
Pb	formation of orthorhombic and tetragonal PbO demonstrated	$Pb(4f)$ and $O(1s)$ spectra	92–94
r.e.	formation of lanthanide (from Tb to Lu-) oxide films demonstrated	shifts in spectra of inner levels	95
Si	stoichiometry and structure of thermally grown SiO_2 films investigated	analysis of $Si(2p)$, $Si(2s)$, and $O(1s)$ spectra	96
–	stability of oxide films in vacuum heat treatment investigated	spectra of inner levels	97
	Bulk-phase oxide specimens		
V	reduction of V_2O_5 to V_4O_9 and V_6O_{11} observed	appearance of $3d$ states in valence band	98
Mn	reduction of α-MnO_2 and β-MnO_2 investigated; only one oxidation state of Mn found in Mn_3O_4	changes in the spectra of the $2p$ level of Mn	99
Fe	the occurrence of reaction $Fe_2O_3 \xrightarrow{CO,\ 300\text{–}460°C} Fe_3O_4$ demonstrated	–1.0 eV shift of $Fe(2p)$ line	100
Co	the reaction $Co(CO_3)_2 \xrightarrow{250°C,\ vacuum} Co_2O_3$ (surface layer contains only Co^{3+} ions) investigated	no satellite in $Co(2p_{3/2})$ spectrum	101
Co	Co_3O_4 surface layer found to contain Co^{3+} and Co^{2+} ions	spectra of inner levels and stretching vibration bands	102
Co	Co^{2+} and Co^{3+} ions identified in Co oxides	$2p_{1/2}$ – $2p_{3/2}$ spin–orbital splitting of Co levels	103
Co	quantitative determination of degree of reduction of Co in $Co_2O_3 \rightarrow Co_3O_4 \rightarrow CoO$ transitions	intensity ratio $I_{cat}/[I_{cat} + I_{Co}.(2p_{1/2})]$	104
Ni	formation of Ni_2O_3 on Ni and NiO surfaces observed	the shift of $Ni(2p_{3/2})$ level is + 1.5 eV in the transition $Ni^{2+} \rightarrow Ni^{3+}$	54
Ni	the formation of $Ni\text{–}O_{ads}$ and $NiO\text{–}O_{ads}$ on bombardment with O_2^+ ions demonstrated	$Ni(2p_{3/2})$ and $O(1s)$ spectra	54,105
Cu	$CuO \rightarrow Cu_2O \rightarrow Cu$ reduction investigated	satellite disappears from $Cu(2p_{3/2})$ spectrum in the $Cu^{2+} \rightarrow Cu^+$ transition	55, 106–108
Ag	$Ag \rightarrow Ag_2O \rightarrow AgO$ oxidation investigated	negative shift observed in $Ag(3d)$ spectrum	109
Pb	Pb in two oxidation states not detected in Pb_3O_4	$Pb(4f)$ spectra	110
Pb	surface composition of Pb_3O_4 found to correspond to $2PbO.PbO_2$	$Pb(4f)$ and $O(1s)$ spectra	92
Cr	$CrO_3 \rightarrow Cr_2O_3$ reduction observed	shift of $2p$ level of Cr	111
Mo	quantitative analysis of MoO_3–MoO_2 mixture	analysis of intensities in $Mo(3d)$ and $O(1s)$ spectra	112
Mo	reduction process $MoO_3 \xrightarrow{400°C,\ H_2} Mo^{6+}, Mo^{5+}, Mo^{4+}$ observed	shifts in $Mo(3d)$ spectra	113,114
Mo	reduction process $Mo^{6+}(MoO_3) \xrightarrow{400°C,\ H_2} Mo^{n+}$ $(n < 4)$ observed	ditto	115
Mo	reduction process $Mo^{6+}(MoO_3) \xrightarrow{400°C,\ H_2} Mo^0$ observed	"	116
Ru	RuO_3 and $RuOCO_3$ detected on the surfaces of RuO_2 and hydrated specimens respectively	analysis of $Ru(3d)$, $O(1s)$, and $C(1s)$ spectra	117
W	$WO_3 \rightarrow WO_2$ reduction observed	analysis of $W(4f)$ spectra	118,119
Re	surfaces of the oxides Re_2O_7, ReO_3, and ReO_2 investigated	analysis of $Re(4f)$ spectra	120
Re	distribution of the density of states in the valence band of ReO_3 investigated	analysis of valence band	121
Al	differences observed in the energies of levels of different modifications of aluminium oxide and hydroxide	analysis of $Al(2p)$ and $O(1s)$ spectra	122
Al	correlation found between E_b for $2p$ level of Al and Al–O distance in aluminosilicates	analysis of $Al(2p)$ spectra	123
–	correlation established between E_b for $O(1s)$ and $1/r$ for M–O bond in 50 oxides	analysis of $O(1s)$ spectrum	124,125
Co, Ni	decrease of E_b for $O(1s)$ with increasing oxidation state of the cation in oxides observed	analysis of $O(1s)$ spectra	126
Fe, Zn	three types of oxygen observed in oxide minerals	analysis of $O(1s)$ spectra	127
–	dependence of shifts of inner levels of metals on the nature of their bond with oxygen in oxides investigated	analysis of $O(1s)$spectra and inner levels of metals	47

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*1 L (1 Langmuir) = 10^{-6} mmHg s^{-1}.

Generalising the experimental data, one may conclude that the most significant information has been obtained about the state of transition metals in the surface layer of oxides. Further studies are probably required to identify the different forms of surface oxygen, using methods sensitive to the nature of the surface oxygen, such as, for example, EPR, optical spectroscopy, etc.

3. Complex Oxides

Regions of homogeneity (solid solutions or chemical compounds) and heterogeneity are as a rule present in two-component variable-composition oxide catalysts. The study of the state of the components in such catalysts and the estimation of surface concentrations are therefore of considerable interest. Quantitative analysis of CuO–MgO, CoO–MgO, CuO–ZnO, and CoO–ZnO systems has been carried out [128,129]. It follows from Fig. 2*a* that in the region of solid solutions in the CuO–MgO system, there is a linear relation between the intensity ratio and the atomic ratio of the components in the bulk of the catalyst. The agreement between the slopes of the experimental and calibration (not shown in Fig. 2) lines indicates the similarity of the surface and bulk-phase compositions [128]. On passing to the heterophase system, the straight line shows a break. Enrichment of the surface in the region of solid solutions has not been observed for CoO–MgO specimens, whereas in CoO–ZnO the surface concentration of cobalt is somewhat higher than the bulk-phase value. No changes in the spectra of the inner levels of the metals after the alteration of the concentrations of the components have been observed [128,129]. It has also been noted [130] that the E_b for the $2p_{3/2}$ levels of cobalt, copper and nickel in the $M_xMg_{1-x}O$ systems do not change, but the ratio of the intensities of the satellite and the peak and the half-widths of the Co^{2+} and Cu^{2+} levels in the catalyst are smaller than in CoO and CuO respectively. In contrast to the above studies, an increase of E_b for the $2p_{3/2}$ level of cobalt by 0.5–0.6 eV has been observed[131] at the 11.3% CoO–MgO concentration, which was accompanied, according to magnetic susceptibility measurements, by an increase of the magnetic moment of cobalt ions. The authors believe that this is caused by the absorption of oxygen in a paramagnetic form, which results in electron transfer from Co^{2+} to O_2.

In $Li_xNi_{1-x}O$ catalysts ($0 \leq x \leq 0.3$) the addition of lithium leads only to a change in the profile of the $Ni(2p_{3/2})$ and O(1*s*) lines[132]. More significant changes in the spectra were observed for $NiO–Al_2O_3$ specimens (Fig. 2*b*). In catalysts with a high NiO content (97.5 and 95%) E_b for $Ni(2p_{3/2})$ is close to the value observed in NiO. However, the shoulder in the spectrum characterising the multiplet splitting is absent for these specimens. With decrease of the NiO concentration to 40 mole %, E_b increases by 1.6 eV and becomes close to the value for the $NiAl_2O_4$ spinel. In the region of solid solutions (0–15 mole % NiO), there is a further increase of E_b, apparently characterising the increase of the effective charge of Ni ions. As in the study of Boreskov and Zhdan[128], the dependence of the line intensity ratio on concentration was obtained in the form of a broken straight line with the break point in the region of the transition to the heterophase system (Fig. 2*b*). A change in the slope of the straight line may be caused by the change in the surface concentrations of the components or the ratio of the particle sizes.

Catalysts obtained by the joint treatment of the La_2O_3–Cr_2O_3 oxides at 750°C have been investigated[133]. For the ratio $La_2O_3 : Cr_2O_3 = 3:1$, chromium is almost completely oxidised to Cr^{6+}, while for the 1 : 1 ratio approximately 50% of chromium remains in the form of Cr^{3+}. The $Mg_{1-x}Cu_x.Al_2O_4$ three-component system has been studied by a number of methods: XPES, secondary ion mass spectrometry (SIMS), EPR, and others[134]. It follows from SIMS data that, after heat treatment at 900°C in air, the system has only the spinel structure. In the spectra of specimens with a low copper content, the O(2*p*) signal is split into two peaks and, with increase in the copper content, the higher energy peak remains unchanged either as regards energy or intensity, while the intensity of the lower energy peak increases and it is displaced towards lower values of E_b. The set of data obtained led to the conclusion that an increase of the copper content results in a delocalisation of the copper electrons, which is the cause of the decrease of the activity of the catalyst in the oxychlorination of ethylene.

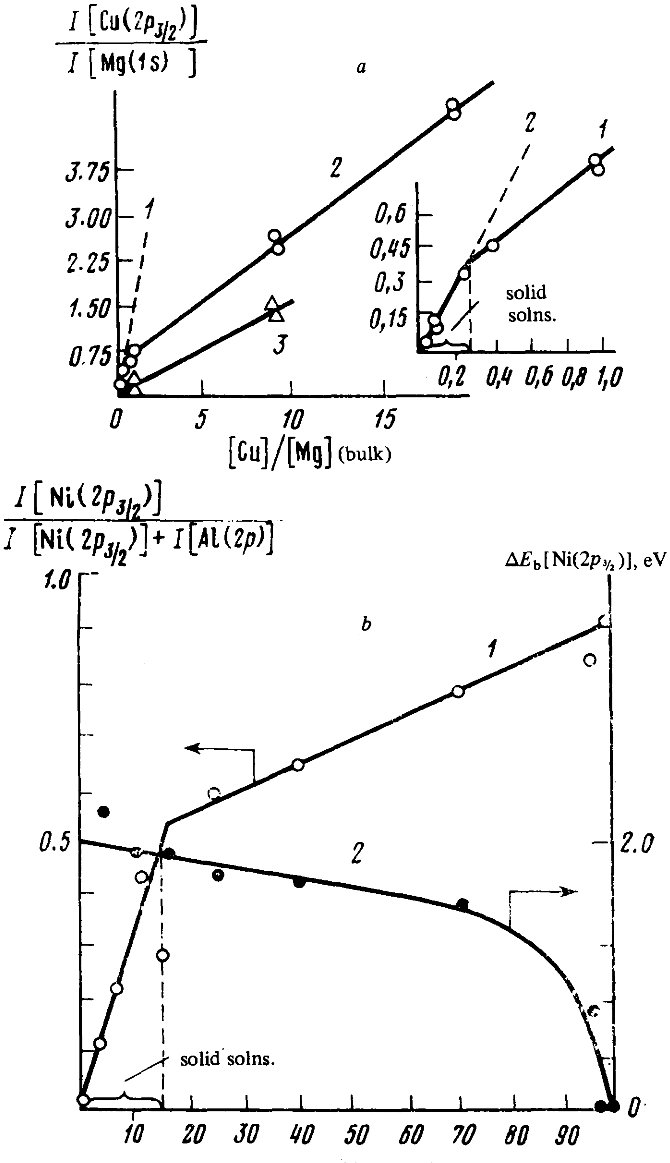


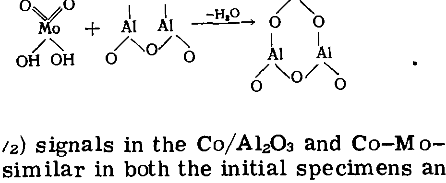
Figure 2. Dependence of the spectroscopic characteristics of the elements (the intensity ratios and the inner level bond energies) on the composition of oxide catalysts: *a*) CuO–MgO[128] [1) and 2) catalysts (curves *1* and *2* represent the solid solution and heterogeneous regions respectively); 3) mechanical mixture]; *b*) $NiO–Al_2O_3$ [1) dependence of the intensity ratio on composition; 2) dependence of the $Ni(2p_{3/2})$ line shift (relative to the NiO line) on composition].

4. Deposited Catalysts

In the study of catalysis on deposited catalysts, information about the nature of the interaction of the active components with one another and with the carrier, about the surface compounds, and about the valence state and concentration of the deposited component is of significant interest for investigators. Depending on the state of the deposited component in the active form, deposited catalysts may be divided into two groups: oxides on carriers and metals on carriers.

(a) Oxides on carriers. Starting with the study of Miller et al.[135], investigators drew attention to the fact that the spectra of deposited cations giving rise to oxides or oxide compounds after heat treatment differ from those of the cations in the corresponding individual compounds. The lines due to the elements in the spectra of catalysts are appreciably broadened and in certain cases chemical shifts are also observed. The magnitude of the observed effects depends on the type of cation and carrier and the method of preparation and treatment of the specimen. The usual scheme followed in the study of such catalysts therefore involves a comparison of the spectra of the catalysts, after various types of treatment or catalysis, with the spectra of the individual oxides, and with those of the postulated bulk-phase analogues of the surface phases and the estimation of the relative surface concentrations.

The most important results were obtained in a study of molybdenum catalysts, which have practical importance. These include in the first place data obtained in the investigation of the alumina–cobalt–molybdenum catalyst for the elimination of sulphur from petroleum, the binary deposited Co/Al_2O_3 and MoO_3/Al_2O_3 catalysts, and the non-deposited cobalt and molybdenum sulphide catalysts, which to some extent simulate the structure of the Co–Mo–Al_2O_3 surface layer, after various types of treatment, or the hydrodesulphurisation reaction in hydrocarbons. In a study of MoO_3/Al_2O_3 Miller et al.[135] observed for the first time a broadening of the Mo(3*d*) line, which was attributed to a donor–acceptor interaction of MoO_3 with the carrier. Other workers reached the same conclusion[114,115,136]. When (3% MoO_3)/Al_2O_3 was reduced, Mo^{6+}, Mo^{5+}, and Mo^{4+} ions were detected[114], oxidation in air resulting in a decrease in the concentration of Mo^{5+} ions, while that of Mo^{4+} ions remained unchanged. The reduction of Mo^{6+} ions in MoO_3/Al_2O_3 proceeds with much more difficulty than in the MoO_3/SiO_2 catalyst owing to the stronger interaction of molybdenum with Al_2O_3. The intense interaction of molybdenum with the carrier persists also in the ternary system[115,136–138]. This is indicated particularly by the finding that the reduction of MoO_3 at 400–500°C in hydrogen leads to the formation of metallic molybdenum, while only Mo^{5+} and Mo^{4+} ions are formed in the Co–Mo–Al_2O_3 system[115,136,138], and, even after prolonged treatment in hydrogen[138] at 500°C, approximately 25% Mo^{6+} remains unreduced. A study of the reduction kinetics showed[138] that Mo^{5+} ions behave as intermediate species in the $Mo^{6+} \rightarrow Mo^{4+}$ transition; the Mo^{5+} concentration on the surface exceeded by a factor of 5 that observed by EPR. The similarity of the Mo(3*d*) bond energies in Co–Mo–Al_2O_3, $Al_2(MoO_4)_3$, and MoO_3 precludes a conclusion in favour or against the formation of aluminium molybdate on the surface. It is noteworthy that XPES data do not appear to conflict with the reaction mechanism adopted in the literature[138].



The Co($2p_{3/2}$) signals in the Co/Al_2O_3 and Co–Mo–Al_2O_3 catalysts are similar in both the initial specimens and after heat treatment at 600°C and apparently correspond to Co^{2+} ions[136,138,139]. We may note that the peaks with E_b = 781.4 and 780.5 eV for Co($2p_{3/2}$) were assigned to cobalt in Co_2AlO_4 and CoO respectively, while the satellite peak with E_b = 784.9 eV was erroneously assigned to Co^{2+} ions coordinated to H_2O molecules. The decrease of the spin–orbit splitting of the $2p_{1/2}$ and $2p_{3/2}$ cobalt sublevels[103] after the heat treatment of (5–10% Co)/Al_2O_3 led to the hypothesis that the cobalt on the surface exists in the tervalent state, although X-ray diffraction revealed the presence of the $CoAl_2O_4$ phase. Analysis of the satellite structure of the spectra of the variable-composition Co–Mo–Al_2O_3 system[140] (0.5–0.6% Co, 2–10% Mo) led to the conclusion that at low concentrations the tetrahedral centres in Al_2O_3 are occupied solely by Co^{2+} ions, while after the formation of the monolayer the Co_3O_4 phase appears. Although, in view of some discrepancy between the results, one cannot postulate an unambiguous form of the surface compound of cobalt and alumina, it is evident that such a complex exists. This is also indicated by the difficulty of reducing Co^{2+} by hydrogen in deposited catalysts.

The problem of the interaction of cobalt and molybdenum in the cobalt–molybdenum–alumina catalyst is no less complex. The authors[141] believe that, with increase of the cobalt concentration to 1% (to give a ratio Mo : Co $\leq$ 4), a phase designated as Mo_4Co is formed on the surface. When the ternary system is heat-treated in air at 600°C, the ratios of the integral intensities of the Co and Al, Mo and Al, and Co and Mo pairs of signals change, which indicates an enrichment of the surface in molybdenum ions and a decrease of the surface concentration of cobalt ions[136]. Reduction of the specimen leads to the opposite effect[115,136]. A smaller cobalt and molybdenum signal intensity ratio in Co–Mo–Al_2O_3 compared with CoO/Al_2O_3 for the same bulk-phase CoO concentrations may be attributed to the fact that cobalt ions are located in deeper layers of the catalyst than molybdenum ions[115,136]. Thus the different conditions for the reduction of cobalt and molybdenum ions and the variation of their surface concentrations when different types of treatment are employed, as well as the differences between the energies in the $CoMoO_4$ and Co–Mo–Al_2O_3 spectra, show that cobalt and molybdenum interact mainly on the carrier. At the same time, according to some data, molybdenum ions prevent the penetration of cobalt ions into the lattice and the formation of a phase resembling a bulk-phase spinel[136].

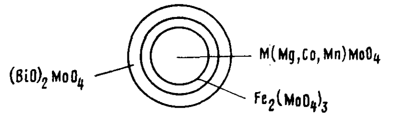
It has been found that the state of cobalt and molybdenum changes significantly in the interaction of the catalyst with model mixtures: thiophen–H_2,[138,142] H_2S–H_2,[138,139] and CS_2–H_2.[143] A general conclusion arrived at in these studies is that cobalt and molybdenum are vigorously, although not completely, converted into sulphides. As regards the identification of the surface sulphides, reliable data on E_b for the electrons of cobalt and molybdenum in sulphides of different composition are necessary. It has been found[143–145] that in contrast to the oxides MoO_2 and MoO_3 the transition from the lowest to the highest molybdenum sulphide entails a negative shift of the Mo(3*d*) line. Furthermore, two S(2*p*) components (with an intensity ratio of 1 : 2), having E_b = 162.9 (S^0) and 161.8 eV (S^{2-}) were observed in MoO_3. This shows that MoS_3 is formed by the association of subcrystalline MoS_2 and amorphous sulphur. A similar conclusion was reached in another study, where Co–Mo–Al_2O_3 deposited catalysts were investigated. Reliable information[146,147] for the Co–S systems was not obtained in the above investigations, because specimens with low cobalt contents were studied [Co/(Co + Mo) < 0.1].

The NiO–WO_3–Al_2O_3 catalyst, which is an analogue of the cobalt–molybdenum–alumina catalyst, has been studied in detail[148]. In the oxide form of the specimen nickel is present as Ni_2O_3 and $NiAl_2O_4$, while W forms a stable complex with γ-Al_2O_3. Nickel is comparatively readily reduced in H_2 to zerovalent nickel, while tungsten remains in the form of W^{6+}. Treatment with thiophen–H_2 and particularly H_2S–H_2 mixtures leads to the formation of sulphides: WS_2 and Ni_3S_2 and NiS. Since the ratio of the nickel and aluminium signal intensities increases under these conditions, it is suggested that nickel sulphides are dispersed on the alumina surface and possibly on the surface of WS_2. We may note that, in contrast to $Co-MoO_3-Al_2O_3$, the $NiO-WO_3-Al_2O_3$ system is almost completely converted into sulphides under these conditions.

Thus XPES yielded information about the state and distribution of molybdenum and cobalt (or nickel and tungsten) ions in the structures of oxide and reduced catalysts and catalysts converted into sulphides. The model of the sulphur-elimination catalyst put forward in a number of studies [149–151], where the ions of the active component exists in the form of a monolayer and those of the promoting agent enter the tetrahedral Al_2O_3 centres, is in general confirmed by these results. At the same time, no evidence has been obtained for the presence of Mo^{3+} (W^{3+}), which are believed [149] to enter into the composition of the active centre, and no data supporting the formation of so-called "incorporated" structure have been obtained [149–151].

The influence of the nature of the additives on the structure of the $V_2O_5-MoO_3$ catalyst has been studied [152,153]. In the NaH_2PO_4 concentration range between 0 and 5% the ratio of the surface concentrations [V]/[Mo] changes by a factor of 4, while the bulk-phase ratio remains constant [152]. When the oxides of various elements were added to the $V_2O_5-MoO_3$ solid solution, a change in the degree of reduction of vanadium ($V^{4+} \rightarrow V^{5+}$) and in the [V]/[Mo] (surf.) ratio was observed. After the introduction of promoting additives into the $CoMoO_4$ α-phase, the bond energies in the cobalt and molybdenum spectra change little [154]. However, when V_2O_5 was deposited on the $CoMoO_4 + MoO_3$ surface using the layer-by-layer method, then the values of E_b for the $Co(2p_{3/2})$ level (+0.6 eV) of [Co]/[Mo] (surf.) increased with the concentration of the additive [154]. This is due to the formation of a $V_2O_5-MoO_3$ solid solution, having the same structure as $CoMoO_4$, and the increase of the charge on cobalt.

An interesting attempt at a layer-by-layer analysis of MCM catalysts (bismuth and iron molybdates with added magnesium, cobalt, and manganese) was undertaken [155]. The iron signal was not detected in the spectrum of the surface layer of the initial specimen. However, after bombardment with Ar^+ ions the surface was depleted in molybdenum and bismuth ions [under certain conditions, the intense $Bi(4f_{7/2})$ peak fully disappeared], whereupon the $Fe(2p_{3/2})$ signal appeared and its intensity increased. On the basis of these results, the following three-layer model was proposed for MCM catalysts:



It is not clear whether the possibility of the migration of the components on the surface during the bombardment with Ar^+ has been taken into account in the above study. The interaction of Bi_2MoO_6 with H_2 led to the reduction of Mo^{6+} to Mo^{4+} [156] and the UPE spectra indicated the formation of two types of donor levels above the valence band; in the last stages of the reduction process some of the bismuth was converted into Bi^{3+}.

Among deposited metal carbonyl catalysts, the $Mo(CO)_6/\gamma-Al_2O_3$ catalyst heated *in vacuo* at 400°C was investigated; molybdenum in the $0 < n < 6$ state was detected in the catalyst [157]. It has already been stated that many deposited oxides react vigorously with the Al_2O_3 surface. In addition it has been shown [158] that heat treatment of catalysts containing zinc and nickel nitrates on the $\gamma-Al_2O_3$ surface leads to an increase of the binding energy in the spectra of the metals by 1 eV relative to the oxides and to a decrease of the $Al(2p)$ binding energy by 0.7 eV. The similarity of the E_b values in the spectra of deposited cations and the corresponding aluminates led to the hypothesis that the latter are formed on the surface of the carrier. A similar conclusion was reached for CuO/Al_2O_3 [159] and WO_3/Al_2O_3. [160] It is believed [103] that the strength of the interaction of CoO with the carrier increases in the sequence $SiO_2 < \gamma-Al_2O_3 < La_2O_3$, $LaCoO_3$ being formed in the last system.

The surface composition of alumina–chromium oxide catalysts (ACC) depends on the nature of the aluminium compound chosen as the carrier [161]. The ratios of the intensities of the $Cr(2p)$ and $Al(2s)$ lines for the catalysts obtained by impregnating bayerite, boehmite, and $\gamma-Al_2O_3$ with the same amount of CrO_3 and heat-treated at 700°C are similar, while the ratio for hydrargillite is higher by a factor of 2. With certain assumptions, the ratio $I(Cr)/I[(Cr) + (Al)]$ may serve as a measure of the specific surface of Cr_2O_3 in ACC. [161] The state of the chromium ions in ACC depends on the chromium content [162]: at low concentrations Cr^{6+} ions were detected in the heat-treated specimens, and, as the chromium concentration increased, the Cr^{3+} phase appeared. The change in the splittings of the $Cr(2p_{1/2})$ and $Cr(2p_{3/2})$ lines and their shift (−1.7 eV) relative to the Cr^{6+} spectrum show that almost the entire chromium is reduced under mild conditions to Cr^{5+}. In the above study and elsewhere [112,163] attention was drawn to the possibility of the photochemical reduction of Cr^{6+} on the surface of carriers. Data [113,164] for the change in the surface composition of CrO_3/SiO_2 catalysts conflict with one another. A sharp decrease in the ratio of the $Cr(2p)$ and $Si(2p)$ signal intensities has been observed [112] as a function of the heat treatment temperature and was explained by the agglomeration of chromium into large Cr_2O_3 particles. On the other hand, the sharp increase of the Cr and Si signal intensity ratio was attributed to the formation of a dispersed $\alpha-Cr_2O_3$ phase on the SiO_2 surface [164]. According to our data, the ratio of the $Cr(2p_{3/2})$ and $Si(2s)$ signal intensities in the non-heat-treated (5% CrO_3)/SiO_2 specimen is higher by a factor of 2 than in the specimen heat-treated at 550°C. In addition, it has been shown [164] that the reduction of CrO_3/SiO_2 to cobalt *in situ* leads to a negative shift of the $Cr(2p_{3/2})$ line by 0.7 eV, which can be explained by the formation of Cr^{2+}. An AlF_3 surface complex on $\gamma-Al_2O$ has been observed [165]. This result as well as data for the interaction of HF with alumina [166] may be of interest for the study of catalysts in which the carrier is fluorinated Al_2O_3.

(b) Deposited metal and "grafted" catalysts. The principal trend in the application of the method to these systems involves the study of the interaction of metal clusters with the carrier, of the degree of reduction of metals, and of the nature of their distribution on the surface. As an example, Fig. 3 presents certain data for the Re/SiO_2 and $Re/\gamma-Al_2O_3$ catalysts [120]. The spectra of the catalysts obtained by impregnating $\gamma-Al_2O_3$ with NH_4ReO_4 and $HReO_4$ solutions differ greatly from those of Re_2O_7 or NH_4ReO_4. An appreciable broadening of the $Re(4f)$ lines and a positive shift are observed for the catalyst. To a lesser extent, this is also seen for the Re/SiO_4 specimens. The reduction of the catalysts in a stream of H_2 at 500°C leads to the appearance of a spectrum which also differs from that of the compact metal. We may note that, according to the results of chemical analysis, rhenium is almost completely reduced to the zerovalent state. The positive shift in the Re($4f_{7/2}$) spectrum relative to the Re^0 spectrum changes as a function of the type of compound used for impregnation: $KReO_4(0) <$ NH_4ReO_4 (0.3 eV) $<$ $HReO_4$ (0.5 eV) $<$ $Ba(ReO_4)_2$ (1.1 eV). The main effect for all the Re/SiO_2 specimens consists in a broadening of the lines. The differences between the spectra of the deposited and compact metal are apparently due to the donor–acceptor interaction between the highly dispersed rhenium particles and the carrier. The broadening of the lines may indicate an energetic inhomogeneity of the rhenium atoms on the surface.

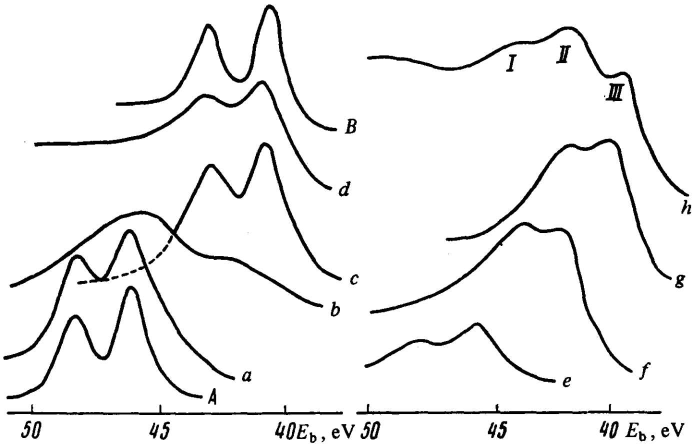


Figure 3. Re($4f$) photoelectron spectra of deposited Re/γ-Al_2O_3 and Re/SiO_2 catalysts[120]: *a*) initial Re/SiO_2; *b*) Re/SiO_2, 300°C, H_2, 10 mmHg; *d*) Re/SiO_2, 200°C, $C_6H_6 + H_2$, 30 atm; *e*) initial Re/γ-Al_2O_3; *f*) Re/γ-Al_2O_3, 500°C, H_2, 10 mmHg; *g*) Re/γ-Al_2O_3, 650°C, H_2, 10 mmHg; *h*) Re/γ-Al_2O_3, 200°C, $C_6H_6 + H_2$, 300 atm; A = NH_4ReO_4; B = Re(metal), 480°C, H_2, 10 mmHg. The I, II doublet characterises Re^{n+} (n = 3 or 4) and the II, III doublet characterises Re^0.

The differences between the spectroscopic characteristics of the deposited and bulk-phase metals have been pointed out in a number of studies: for Ir[167-169], Pt,[170-173] Pt–Ge,[173] Pt–(Mo, W, Re),[174-176] W,[178] Rh,[179] and Pd.[45] The chemical shift of the Ir($4f$) line[169] relative to Ir^0 changes as a function of the nature of the carrier: ZnO (0.3 eV) $<$ SiO_2 (0.9 eV) $<$ α-Al_2O_3 (1.0 eV) $<$ TiO_2 (1.2 eV) $<$ δ-Al_2O_3 (1.8 eV) $\leqslant$ aluminosilicate. The appearance of the shift is caused, according to the authors[169], by the equalisation of the positions of the Fermi level on the surfaces of different oxides. The broadening of the Pt($4f$) line and the appearance of an additional peak near the Fermi level has been interpreted[170] as a consequence of the interaction of Pt clusters (whose size is d = 12–20 Å) with silica gel. Similarly, a broadening of the Pd($3d$) line and a small positive shift relative to the Pd^0 spectrum have been observed for Pd/Al_2O_3.[45] In addition there is a decrease of the density of states in the vicinity of the Fermi level. Calculation with the aid of the extended Hückel method showed that the interaction of the palladium atom with the γ-Al_2O_3 surface may lead to similar changes in the spectra. According to an alternative explanation, the effects observed in the spectra of deposited metals are due to the anomalous electronic properties of the metallic clusters. The most interesting attempt to follow the changes in the spectrum in the valence region for different surface coverages by metal atoms was undertaken by Mason and coworkers[171,180] and Hamilton[181]. For low surface coverages of graphite by silver, the spectra of the valence bands show that the *sp* band of silver atoms is unfilled and that there is a small peak with $\Delta E\Phi = -2$ eV. Calculation by the CNDO method showed that such states are characteristic of Ag_1–Ag_4/C_{16} clusters[180]. With increase of the degree of surface coverage, the spectrum characteristic of metallic silver gradually appears.

The nature of the clusters and their interaction with carriers can in principle be inferred from XPE spectra. However, it is first necessary to solve a number of complex problems: (1) one must find a method of separating chemical relaxation shifts and shifts caused by the matrix effect. The difficulty is that the charging of the inhomogeneous surface of the specimen can also cause a broadening and distortion of the lines. More direct results can be obtained by studying the UPE and XPE spectra of the valence bands. (2) One must find a method of isolating the components responsible for the alteration of the electronic properties of the clusters and for the interaction with the support. For this purpose, it is necessary to study the clusters on inert carriers and to compare the experimental data with calculation. In view of the foregoing, studies on "grafted" catalysts, particularly on organic carriers, on which it is possible to obtain clusters with rigorously specified dimensions, appear promising. At the present time there have been few investigations, in which only metals grafted via π-allyl complexes to the silica gel surface were investigated[174-178]. In the presence of low-valence molybdenum, tungsten, and rhenium ions, the electron density of platinum diminishes[174-178]. The enhancement of the interaction of tungsten grafted to the SiO_2 surface relative to the standard specimen obtained by impregnation is indicated by the results of Shul'ga et al.[178]

It has been suggested[172] that, after the impregnation of alumina with H_2PtCl_6 and reduction, some of the platinum atoms are coordinated to chloride ions and Al_2O_3, i.e. are formally in the quadrivalent state. The state of a rhodium complex deposited on a polymer has been characterised[182]: E_b for Rh($3d$) in the catalyst was close to the value for the initial complex $RhCl_2[P(o\text{-tolyl})_3]_2$. A change in the valence state of rhodium was not observed after prolonged exposure of the specimen to air. After treating SiO_2 with hydrogen at 800°C in the presence of metals (Ni, Pt, Ta, and W) but without physical contact with them, the Si–OH groups were reduced to Si–H groups, which, judging from the XPES data, is due to transfer of traces of metals to the surface[183].

In a heterophase system the expression for the intensity ratio may be represented as follows[184]:

$$\frac{I_M}{I_C} = \frac{I_M^\infty}{I_C^\infty}\,\frac{f\,[1 - e^{-c/\lambda_M(E_M)}]}{1 - f\,[1 - e^{-c/\lambda_M(E_M)}]}\,, \tag{6}$$

where I_M^∞ and I_C^∞ are the signal intensities in the spectra of infinitely thick metal and carrier specimens, f is the fraction of the surface occupied by the metal, c the size of the metal crystallites, and λ_M the mean free path of electrons with a kinetic energy E_M. Thus, together with concentration, the surface coverage by the metal and the size of its crystallites influence the intensity ratio. Evidently in the two extreme cases (where $c \ll \lambda$ and $c \gg \lambda$) with homogeneous coverage, a linear relation should be observed between I_M/I_C and the metal concentration. Indeed, a direct correlation has been noted[184,185] between the ratio I(Pt)/I(Si) and the characteristics of the platinum surface, namely the volume of absorbed H_2 and the ratio of the number of Pt atoms, i.e. [Pt], to the specific surface of the carrier S_{sp}. For highly disperse systems (Pt/SiO_2 and Na/Al_2O_3), the composition determined with the aid of XPES is close to that of the bulk phase. For specimens with a lower degree of dispersion, a direct relation is observed only when I(Pt)/I(Si) is plotted against [Pt]/cS_{sp} (Fig. 4).

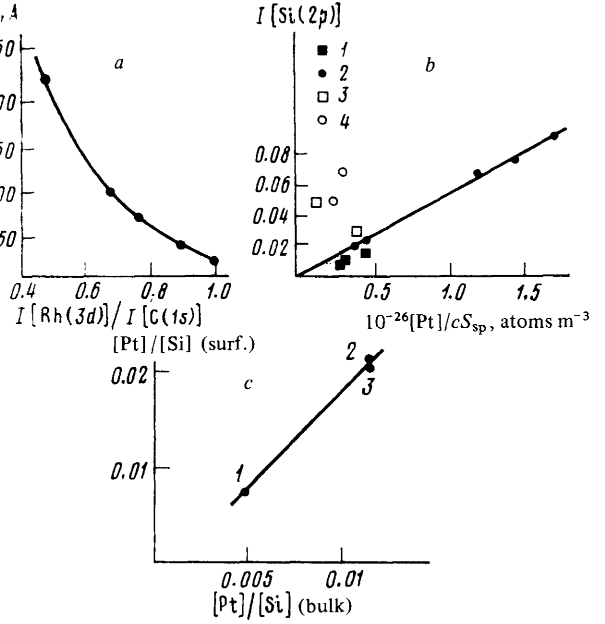


Figure 4. The influence of the particle size of the metal and of its surface concentration on the metal : carrier signal intensity ratio in the spectra of catalysts with deposited metals: *a*) dependence of the ratio $I[\mathrm{Rh}(3d)]/I[\mathrm{C}(1s)]$ on the particle size of Rh^0 in the catalyst [(12 wt.% Rh)/C];[186] *b*) dependence of the intensity ratio $I[\mathrm{Pt}(4f)]/I[\mathrm{Si}(2p)]$ on the surface concentration of platinum [see Eqn. (6)] in Pt/SiO_2 catalysts[184,185] [1) and 2) specimens prepared by ion exchange; 3) and 4) specimens prepared by impregnation]; *c*) dependence of the surface concentration of platinum {determined by analysing the $I[\mathrm{Pt}(4f)]/I[\mathrm{Si}(2p)]$ ratio} on the total amount of platinum in Pt/SiO_2 specimens [1) (1.2 wt.% Pt)/SiO_2, ion-exchange method; 2) (3.5 wt.% Pt)/SiO_2, ion-exchange method; 3) (3.5 wt.% Pt)/SiO_2, impregnation method].

According to the results of Shul'ga and coworkers[178], a linear relation between I(W)/I(Si) and the tungsten content is characteristic both of specimens obtained by impregnation and of "grafted" catalysts. However, the increase of the slope for specimens of the latter kind indicated a higher degree of surface coverage by tungstate (higher by a factor of 20 than for the "impregnated" specimens). According to our results, the ratio [Pt]/[Si](surf.) (Fig. 4) found from the XPE spectra exceeds the average bulk-phase value. Subsequent heat treatment and reduction of the specimen led to a decrease of the ratio of the Pt and Si signal intensities. One of the causes of this is the increase in the size of the metal particles.

Similar phenomena in the spectra have been observed in other studies[120,172,173,186,187]. Thus, with increase of the size of the Rh^0 crystallites in the (12% Rh)/C catalyst from 20 to 235 Å (λ = 18 Å), the intensity ratio $I[\mathrm{Rh}(3d)]/I[\mathrm{C}(1s)]$ decreases by a factor of two[186] (Fig. 4). With increase in the size of the platinum crystallites from 10 to 25 Å in the (1.2% Pt)/SiO_2 ion-exchange specimens, a decrease of the Pt and Si signal intensity ratio by a factor of 1.8 was observed, and a slight decrease of the degree of dispersion of the metal (from 50 to 60 Å) in Pt/SiO_2 specimens obtained by impregnation resulted in an appreciable decrease of the intensity ratio (by a factor of 3). These data show that the change in intensities is caused not only by the change in the degree of dispersion, but also by a redistribution of the metal atoms on the surface. In consequence of the inhomogeneous distribution of the metal in the "impregnated" specimens, there is a possibility of a transition of metal atoms from pores more accessible to analysis to less accessible regions[184,185]. Clearly the ratio of the metal and carrier signal intensities may depend, other conditions being equal, on the porosity of the carrier, which has in fact been observed experimentally[188,189].

5. Zeolite Catalysts

The study of the state of elements in the surface layers of zeolites may be of considerable interest for the selection of conditions in the formation and operation of zeolite catalysts. Such information is important also because certain catalytic reactions apparently occur only in surface layers of zeolite crystals.

(a) Zeolites not containing transition metals. Fig. 5 presents the dependence of the ratio I(Al)/I(Si) on the zeolite modulus obtained in a number of studies[23,190-193]. In all cases the relation is linear. However, the calculations of [Al]/[Si](surf.) carried out in these studies indicates a discrepancy between the experimental results. According to some data[23,193], within the limits of experimental accuracy and the assumptions made, the compositions of the surface and bulk-phase of A, X and Y zeolites and mordenite are similar. Systematic elimination of aluminium from the surface of zeolites of these types has been pointed out[190-192]. The ratio [Al]/[Si](surf.) increased when the zeolite structure was disrupted[197]. The lower Al and Si signal intensity ratio found by Tempere and Delafosse[190] cannot be explained by the shielding of the Al^{3+} ions by water or by other cations, because changes in these factors do not alter the intensities[196]. The discrepancies between the experimental data are probably due to the non-equivalence of the specimens used in different investigations[23,190-193]. Comparison of the Ca and Si signal intensity ratios for (NaCaA) and Na/Si(HNaY) (Fig. 5) with the degrees of exchange of the corresponding cations shows that non-transition metal ions are apparently uniformly distributed in the zeolite structure. With increase of the SiO_2/Al_2O_3 ratio, the energies of the Al lines do not change and are similar to those in

Al_2O_3, while the Si(2p) line shifts by 0.7 eV and the energy of the Si(2p) bond approaches the value observed in SiO_2.[191] These data conflict with those[123] for natural aluminosilicates where a correlation was found between the shift of the Al(2p) line and the average Al–O distance.

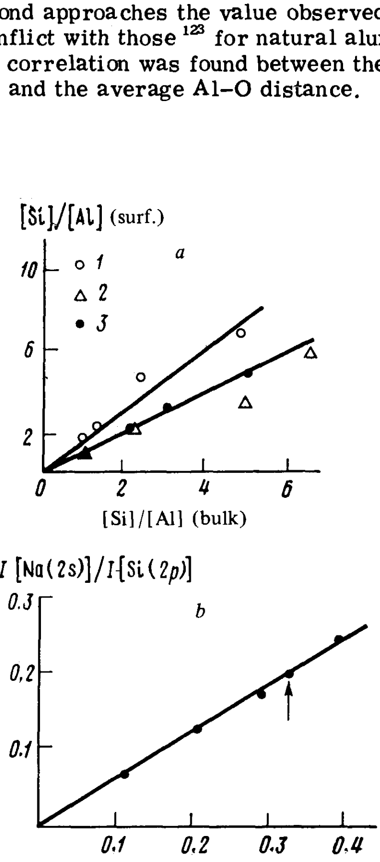


Figure 5. Composition of the surface layer of zeolites. a) dependence of the ratio of the numbers of silicon and aluminium atoms in the surface layers of zeolites (XPES data) on the ratio of the total numbers of these atoms in the zeolites [1) data of Temperet et al.[191]; 2) data of Finster and Lorens[193]; 3) present authors' data]; b) dependence of the intensity ratio I[Na(2s)]/I[Si(2p)] on [Na]/[Si] in the "bulk" of partly "decationated" type Y zeolites. For the specimen marked with an arrow, [Na]/[Si](bulk) = 0.32 [Na]/[Si](surf.) = 0.39.

With increase of the degree of exchange of Na^+ for Ca^{2+} from 20 to 80%, a positive shift (0.5 eV) of the Ca(2p) line is observed, apparently characterising the increase of the effective charge on calcium[40]. Comparison of the positions of the Na, K, Ca, and Mg lines in the spectra of zeolites and compounds with different types of chemical bonds permits the conclusion that the cations form predominantly ionic bonds with the zeolite skeleton[23,40]. A similar conclusion was reached in other studies[194,195] for magnesium ions in MgNaX and MgNaY.

According to some data[192,196], the adsorption of pyridine on the HY zeolite at 150°C led to the reduction of surface silicon ions to the elemental state. This result is not altogether understandable from the standpoint of the thermodynamics of the reduction of silicon and apparently requires further confirmation. The adsorption of pyridine at room temperature can be used as a test for quantitative estimates of the fraction of Brønsted and Lewis acid centres[192,196]. The splitting E[N(1s)] – E[Si(2p)] is 297.4 and 298.3 eV after adsorption on Lewis centres and 299.5 and 300.1 eV after adsorption on Brønsted centres[192]. A study of the adsorption of aniline on the HY zeolite was also undertaken[197].

(b) Zeolites containing transition metals. Systematic studies on individual and polycationic forms of zeolites have been made[23,40,198-205]. Since some of the results obtained have already been published in a review[200], we shall confine ourselves to an examination of certain examples.

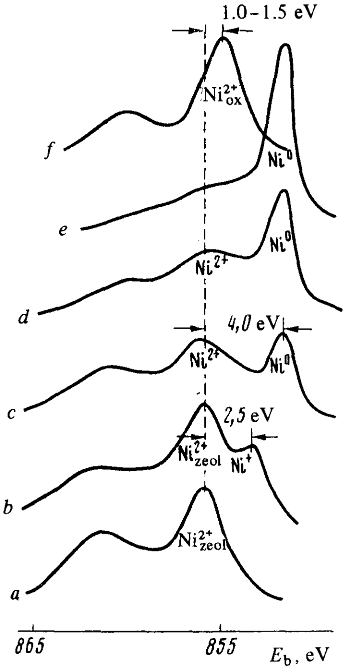


Figure 6. Variation of the valence and physical states of nickel for different methods of treatment of the NiNaY zeolite: a) dehydration, 400°C, air + 500°C, helium; b) 400°C, 10 mmHg CO; c) 350°C, 10 mmHg H_2; d) 400°C; 10 mmHg H_2; e) 450°C, 1 atm H_2 (the spectrum is shown in terms of a 1 : 3 scale); f) 450°C; H_2 + 500°C, air.

Comparison of the parameters of the spectra of Cr, Fe, Co, Ni, and Cu (the positions of the lines and of the satellite structures) in zeolites and in compounds with different types of bonds showed that the amount of ionic character of the cation–zeolite skeleton bond is close to that in fluorides or chlorides[40,203]. The capacity of cations for reduction depends on the nature of the transition metal[40,198-203], the type of structure[40,201], the degree of exchange[40,200,201], and the cationic composition[40,201-203]. As an example of the possible changes in the state of the elements in zeolites, we shall consider the spectra of Ni(2$p_{3/2}$) in NiNaY, treated under different conditions (Fig. 6). Spectrum a is due to Ni^{2+} ions. After dehydration, the lines characterising the distribution of the ions in regions with different crystal field symmetries are broadened somewhat. The new line in the spectrum with $\Delta E = -4$ eV, appearing after the reduction of the specimen with hydrogen, corresponds to zerovalent nickel. With increased temperature of the heat treatment in hydrogen, the degree of reduction of zerovalent nickel increases, and at high temperatures the ratio of the integral Ni and Si signal intensities increases relative to the initial value. The latter observation demonstrates the diffusion of zerovalent nickel atoms on the outer surface. On treatment in carbon monoxide, a line occupying a position intermediate between those of the Ni^{2+} and Ni^0 lines is observed. It has been attributed to the formation of the Ni^+ ion[204].

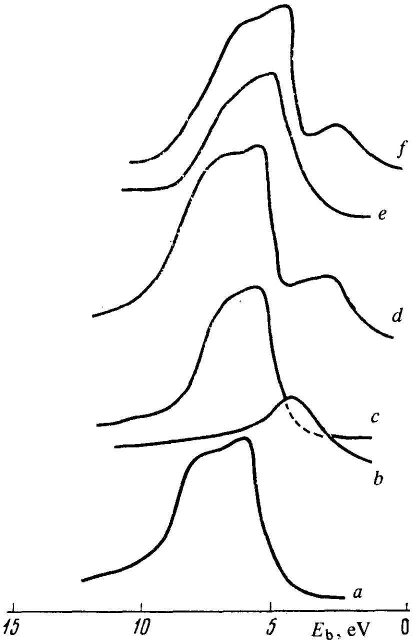


Figure 7. The interaction of metallic silver and copper in zeolites[203]; spectra: *a*) 0.14 AgNaY, 500°C, H_2; *b*) 0.26 CuNaY; 500°C, H_2; *c*) initial 0.25Ag.0.31CuNaY specimen; *d*) 0.25Ag.0.31CuNaY, 350°C, vacuum; *e*) 0.25Ag.0.31CuNaY, 500°C, H_2; *f*) result of the addition of spectra *a* and *b*.

Finally, after the oxidation of reduced Ni-zeolites, the position of the spectral line is close to that observed in the NiO spectrum[198]. This indicates the formation of the oxide phase on the outer surface. Thus XPES makes it possible to obtain information about several valence and phase states of metals in zeolites. Interesting results were obtained in the study of polycationic forms (Ag–Cu, Cu–Ni, Co–Ni, Cr–Ni)[203-205]. In all cases the capacity of cations for reduction and migration changes in relation to individual forms. This is due to the interaction of transition metals with one another. Fig. 7 illustrates the spectra of the valence bands of silver and copper in individual and polycationic forms[203]. Their comparison with one another, and also with the spectrum obtained by adding together curves *a* and *b*, shows that zerovalent silver and copper interact with one another, forming alloys on the outer surface or bimetallic clusters[202,203].

Despite the fact that quantitative analysis in zeolites containing transition metals involves a number of difficulties, one may reach certain important conclusions on the basis of the changes in signal intensities concerning the distribution of transition metals between the outer surface and the bulk of the crystals. The changes in the $Cu(2p_{3/2})$, $Ni(2p_{3/2})$, and $Si(2s)$ lines occurring in the oxidation-reduction treatment of Ni–Cu-zeolites have been investigated[205]. After treatment with hydrogen, the increase of the Cu and Si and of the Ni and Si signal intensity ratios indicates the migration of zerovalent copper and nickel onto the outer surface, while magnetic susceptibility measurements indicate the formation of an Ni–Cu alloy[205]. Oxidative treatment of these specimens causes a decrease of the intensity ratio of the Cu and Si lines, although the absolute magnitude of the $Si(2s)$ signal also diminishes by a factor of two. The decrease of the intensity of the $Si(2s)$ line may be caused by the increased shielding of the surface by metals as a result of their dispersion and hence should lead to an increase of the Cu and Si signal intensity ratio. Since the opposite behaviour is observed, presumably part of the copper diffuses after oxidation to the bulk of the zeolite crystal, which has indeed been confirmed by the appearance of an EPR signal due to isolated Cu^{2+} cations[205]. As for catalysts with deposited metals, the metal distributed in the zeolite may interact with the lattice. It has been stated[206] that E_b for Pt and Pd in zerovalent palladium and platinum clusters, trapped within zeolite cavities, is greater by approximately 1.0 eV than for metallic palladium and platinum, which has been attributed to the transfer of electron density from the metal atoms to the elements of the skeleton and also by a smaller relaxation energy.

In addition, a study has been made of the reduction $Eu^{3+} \rightarrow Eu^{2+}$ in the Eu-form of the zeolite, which is accompanied by an unusually large shift of the 3*d* line of europium (−7.6 eV).[23] The photochemical reduction of nickel in nickel-containing zeolites has been observed[207]. Under the conditions adopted in the measurement of spectra[199-203], this was not observed, although such effects were noted for silver, palladium, and copper cations.

(c) Other catalysts. The surface composition of rhenium heptasulphide has been studied[208,209]: the presence of sulphur in two states (S^{2-} and S^{6+}) was noted. It was shown that the hydrogenating activity of catalysts varies as a function of the ratio of sulphate and sulphide ions. When pyrolytic graphite, with silver sputtered onto the surface of the basal planes as the catalyst, was oxidised[210], no shifts of the Ag(3*d*) lines were observed. The decrease of the intensity of the Ag(3*d*) signal was explained by the agglomeration and evaporation of (Ag). It was noted that, when WC is formed, the density of states near the Fermi level becomes close to that for platinum[211]. This explained the similarity of the catalytic properties of WC and Pt in many reactions.

6. The Surface Compositions and Catalytic Properties of Heterogeneous Catalysts

Together with direct study of the catalytic reactions by the PES method (see below), there are also other procedures for the determination of the relation between the catalytic properties of heterogeneous catalysts and the state of their surfaces.

(a) The influence of the state of the elements on the activities and selectivities of catalysts. An industrial silver catalyst for the synthesis of epoxyethane has been studied[212,213] before and after γ-irradiation. It was shown that irradiation leads to an increase of the concentration of calcium ions on the surface, which entails an increase of the activity of the catalyst. With increase of the oxide/metal ratio in Rh/C catalysts, an increase of their hydrogenating capacity was noted[214]. Comparison of XPES data obtained in the reduction of Ni-, Co-, Ni–Co, Ni–Cu-, Ni–Cr, and Cu-zeolites and the activities of the catalysts in the reactions of carbon monoxide with nitric oxide and molecular oxygen led to the conclusion that the reduction of transition metal ions to the metals entails an appreciable increase of activity[215]. The same conclusion was arrived at for the reaction of carbon monoxide with nitric oxide on NiO, Co_2O_3, and Fe_2O_3.[216] The highest activity among copper(II) oxide catalysts is shown by that containing Cu^+. After the addition of platinum, the catalytic activity of the perovskites $La_{0.7}Pb_{0.3}.MnO_3$ in the oxidation of cobalt increases by a factor of 100. The increase of activity exceeds the effect expected for the homogeneous redistribution of platinum, whose activity corresponds to that of metallic platinum on A_2O_3. XPES data show that platinum is localised in the perovskite lattice in the form of Pt^{4+}.[217]

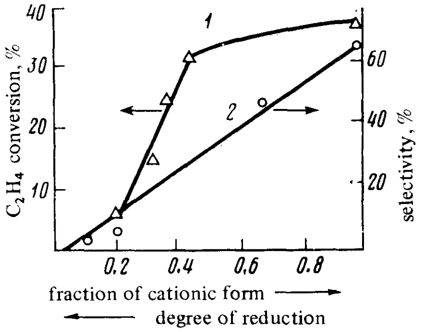


Figure 8. The influence of the state of transition elements on the activity and selectivity of zeolites in hydrocarbon conversion reactions: 1) variation of the degree of conversion of C_2H_4 on PdCaNaY[220] with the degree of reduction of palladium; 2) variation of the selectivity of NiNaY in the synthesis of s-butylbenzene with the degree of reduction of nickel[219].

Comparison of data for the catalysis of the oxidative dehydrogenation of paraffins in the presence of mixtures of nickel and tin oxides promoted by phosphorus and potassium and the results of physicochemical experiments (EPR, XPES)[218] led to the hypothesis that the lattice oxygen is involved in the reaction. The changes in the state of vanadium and of the ratio [V]/[Mo](surf.) in V_2O_5–MoO_3 catalysts promoted by Na_2HPO_4 are correlated with the changes in catalytic activity in the oxidation of furan to maleic anhydride[152]. In the case of $CoMoO_4$ modified by oxides the decisive factor determining the activity in the oxidation of propene and acrolein is the nature of the additive and not the ratio [Co]/[Mo](surf.)[155]. With increase of the fraction of Mo^{4+} bound to sulphur and oxygen in the overall amount of molybdenum in the Co–Mo–Al_2O_3 catalyst, an increase of the yield of CH_4 in the reaction involving the hydrodesulphurisation of CS_2 is observed[143].

The study of Ni- and Pd-zeolites[219,220] showed that the main factor determining the selectivity in the alkylation of benzene by ethylene to s-butylbenzene and the dimerisation of ethylene is the state of nickel and palladium respectively. In both cases cations are active in catalysis and a qualitative parallel relation between the fraction of the cationic form and the catalytic activity is observed (Fig. 8). The data examined show that in many instances a relation has been found between the state of the elements on the surface and the activity. It is also clear that, in order to obtain more far-reaching relations, additional data on the reaction mechanisms are required.

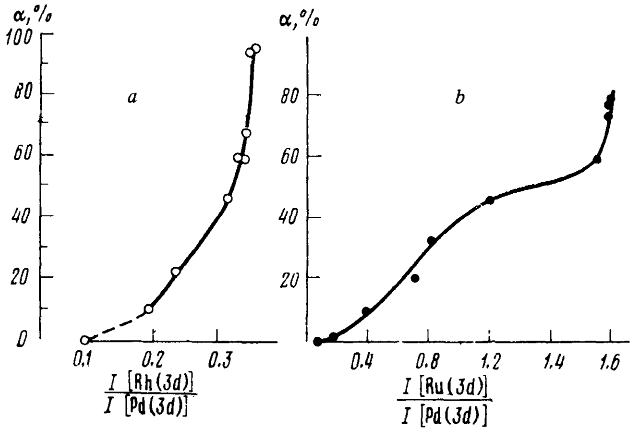


Figure 9. Correlation between the changes in the surface state of palladium alloys and their activity (α is the yield of C_6H_6) in the dehydrogenation of cyclohexane: *a*) Pd–Rh (10% Rh)[221]; *b*) Pd–Ru (10% Ru)[222].

(b) Modification of the surface of the catalysts under the influence of the reaction medium. Modification of the surface layer of catalysts in the reaction medium is characteristic of many specimens and reactions. The surface composition of binary alloys of palladium with rhodium (5 and 10%) and ruthenium (10%) changes only slightly when the catalysts are treated in H_2 and O_2.[82] At the same time the interaction of these alloys with hydrocarbons under the conditions of the dehydrogenation of cyclohexane to benzene leads to an appreciable enrichment of the surface in rhodium or ruthenium. Fig. 9 shows that there is a parallel variation of the catalytic activities of these alloys and of the surface composition[221,222]. It was shown, on the basis of these data and adsorption measurements, that the active surface is formed as a result of the segregation of the second component on the surface and the increase of the roughness of the latter[222]. A study of the initial and spent Pt–Rh catalysts for the oxidation of NH_3 showed that their deactivation is due to the segregation of rhodium on the surface in the form of Rh_2O_3 and Rh^0, which takes place as a result of the volatilisation of oxidised platinum. The activation of the Rh/Al_2O_3 catalyst in the tricyclomerisation of ethylene was accompanied by a positive shift of the Rh(3*d*) line by 0.6–0.8 eV. This was caused by the appearance of a positive charge on rhodium as a result of its interaction with hydrocarbons. Treatment with the $C_6H_6 + H_2$ mixture leads to partial reduction of rhenium in Re/Al_2O_3 catalysts and to the appearance of catalytic activity[126] (Fig. 3). On the other hand, the reduction in ethylene of the zeolite palladium and of its reaction products deactivates the catalyst[220]. The reduction of palladium in the Pd/SiO_2 catalyst in the hydrogenation of hex-1-ene has been pointed out[224].

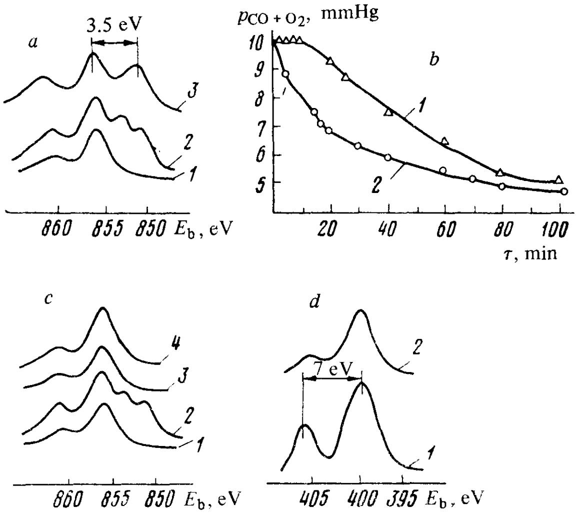


Figure 10. The influence of the state of transition elements on the catalytic activity of zeolites in the oxidation of CO by oxygen and the reduction of NO by carbon monoxide[215]: *a*) lines of $Ni(2p_{3/2})$ in NiNaY [1) dehydrated specimen; 2) specimen treated with CO at 400°C; 3) specimen treated with CO + O_2 at 400°C]; *b*) kinetics of the oxidation of CO on NiNaY at 400°C [1) first experiment; 2) second and subsequent experiments]; *c*) lines of $Ni(2p_{3/2})$ in CuNiNaY [1) dehydrated specimen; 2) specimen treated in CO at 400°C; 3) after subsequent treatment with NO at 400°C; 4) specimen treated in NO + CO at 400°C]; *d*) N(1*s*) lines [1) heat treatment of CuNiNaY in NO + CO at 400°C; 2) heat treatment in NO at 400°C].

Fig. 10 illustrates the changes in the XPE spectra and of the catalytic activity of NiY in the oxidation of carbon monoxide[215]. The interaction of the zeolite with the CO + O_2 mixture under the conditions of the catalysis leads to the reduction of Ni^{2+} to the metallic and possibly the univalent states. The period of the activation of the given specimen is apparently associated with this process. The concentration of Cr^{2+} in Cr/SiO_2 catalysts subjected to preliminary reduction in CO diminishes on subsequent interaction with NO at 300°C.[164] When the specimen is maintained in the NO + CO mixture, Cr^{2+} is reformed. The activity of the complex $ReCl(NO)(Py)_2$ in the hydrogenation of pyridine or cyclohexene was four times greater than that of Re_3Cl_9.[225] According to XPES and infrared spectroscopic data, this is due to the fact that part of the rhenium in the complex retains its coordinate linkage with NO, while the surface layer of the chloride is completely reduced to zerovalent rhenium.

Thus XPES data show that changes in the surface layer under the influence of reaction medium, which may lead to both activation and deactivation of the specimens, are characteristic of catalysts of different types.

The products formed on the surface during the reactions may be investigated with the aid of XPES. The consecutive aldehyde → acid → $CO_2 + H_2O$ transformations on the selective MoO_3, MoO_2, and $CoMoO_4$ oxidation catalysts were investigated at 77–773 K.[226] The interaction of NO with CoO and NiO [227] leads to the appearance of the N(1*s*) peak, whose position indicates electron transfer from the oxide to NO. In the adsorption of nitrogen on Fe_2O_3, the Fe(3*p*) bond energy did not change, while the positive shift of the spectrum of iron in Fe_3O_4 indicated the oxidation of the surface[228]. The two forms of adsorption of NO have been observed to a lesser extent on the surfaces of nickel-containing zeolites after their interaction with NO or NO + CO at 220–550°C.[215] The higher- and lower-energy peaks characterise the formation of the nitrosyl and nitrate complexes respectively. The deactivation of zeolites at low temperatures in the reduction of NO is probably due to the formation of stable nitrate complexes[215] (Fig. 10).

Results obtained by UPE and XPE spectroscopy led to conclusions concerning the mechanisms of the decomposition of HCOOH and the adsorption of pyridine on metallophthalocyanines[229]. The adsorption of pyridine is not accompanied by a change in the charge on iron, while HCOOH dissociates heterolytically with adsorption of the formate ion on the central atom and of the proton on the bridging nitrogen atom in the porphyrin ring.

7. Results of Adsorption Studies

As mentioned above, there is an extensive literature on the application of PES to the study of adsorption[24,25,29–37]. Two international conferences have been devoted to problems associated with the interpretation of the spectra of adsorbates[32,33]. Taking this into account, we decided to give only a brief account in the present review (retaining as far as possible the complete bibliography) of the principal research trends. New results of studies on the adsorption of hydrocarbons and catalytic reactions at low pressure of reactants are described in greater detail.

(a) Adsorption on metals. The study of the interaction of simple gases with metallic surfaces is the main field of application of PES to adsorption. In these systems there is in fact a possibility of obtaining polycrystalline and single-crystal atomically pure surfaces and of deriving the maximum information with the aid of other physicochemical methods.

The interaction of CO with tungsten[230–238], molybdenum[30,232–234,239–241], platinum[232,242–250], ruthenium[248,251–255], palladium[256,257], nickel[232,233,241,249,258–262], iridium[263,264], iron[166,265], copper[232,241,266,267], titanium[268], and cobalt[269] has been studied vigorously. Several forms of adsorption of CO on polycrystalline tungsten have been observed[230,231,238]: The α-form with bonding close to that in carbonyls, which disappears in the temperature range 300–640 K, the dissociative form, and the weakly adsorbed "virgin" state. In molecular adsorption on tungsten, and on other metals, the chemisorption linkage is formed by the $5d$ orbitals with the lone electron pair. A correlation has been observed[232] between E_b for the O(1s) level and the heats of adsorption on five metals, which indicated a contribution of the πd component to the chemisorption linkage. For the strongest adsorption (Ni, Pt, Pd, Ru, Fe), ΔE_b = 2 eV, and for the weakest adsorption (γ = CO/Mo) ΔE_b = −3.2 eV. According to the authors[232], there is a CO dissociation threshold at room temperature: ΔH_{ads} = 260 kJ mole^{-1}. Apart from tungsten (β-form), dissociative adsorption has been observed on molybdenum (β-form)[240], iron[265], nickel[233,261], titanium[268], and copper[266].

Polycrystalline tungsten and platinum do not catalyse the dissociation of NO at temperatures up to 100° C[30,270-272]. Ruthenium[248], iridium[273], nickel[262,274], and iron[275-277] are more active in the dissociation of NO. NO dissociates on the (1010) faces of ruthenium even at 100 K (NO exposure = 1.5 L). The peaks of nitride nitrogen and atomic oxygen in the spectrum of NO adsorbed on the (111) face of iridium are observed at 323–373 K; it has been suggested that oxygen blocks the active centres for the decomposition of NO.[273]

Numerous studies have been devoted to the interaction of O_2 with metal surfaces, and, together with adsorption on reconstructed surfaces, the oxidation of surface layers was investigated, from the initiation of the oxides until the formation of oxide phases. These processes may constitute the individual stages of the reactions with participation of oxygen.

The interaction of O_2 with the surfaces of polycrystalline tungsten[231,265] and the (111), (110), and (100) tungsten faces[238,274,278-280], polycrystalline molybdenum[30,240], platinum[243,248,281], palladium[256], iridium [(100)[263] and (111)[282]], ruthenium [(10$\bar{1}$0) and (001)][253,279,283], polycrystalline nickel[30,232,284-286], nickel (100)[287], polycrystalline silver[288,289], the (100) face of silver[278], polycrystalline copper[266,289-291], the (110)[292] and (100)[293] faces of copper, polycrystalline gold[289], sputtered iron[267,286,294,295], zinc[296], and tin[297], and magnesium, aluminium, chromium, manganese[238], lanthanide[299], cerium[84], titanium[84], and cobalt[269] films.

It has been stated in a report[300], and in a number of reviews[30,32,33,36,37] that the adsorption of oxygen on a number of metals (V, Mn, Fe, Co, Ni, Cu, Ag, Zn, Mo, W, Ru, Ir, Au, and Na) at room temperature leads to the appearance of the O(1s) peak with E_b = 530 ± 0.5 eV (in UPE spectra there is a maximum with $E_b \simeq$ 6 eV). This may indicate a similarity of the structures of the adsorption complexes of oxygen, which are believed[33] to be of "the oxide-like" type. However, it is more likely that the agreement is merely formal and does not reflect the constancy of the charge on oxygen but is caused by the different contributions of the Madelung and relaxation terms to ΔE_b.

At the same time other forms of adsorbed oxygen were also observed: O(1s) signals with 531.4–532.0 eV (Ni, Co, Mn) and 533 eV (Pt) corresponding to them. The adsorption of O_2 on nickel at 300 K and $\theta < 1$ led to the appearance of two O(1s) peaks, one of which was assigned to adsorbed oxygen and the other to oxygen which penetrated underneath the surface of the crystal (531.4 eV). Three types of oxygen were observed in another study[285] in the range 77–500 K ($\theta < 1$) on nickel. Finally, the transition from adsorption to the generation of the NiO phase and the formation of the bulk-phase oxide were observed in the range $0.5 \leqslant \theta \leqslant 2.0$. The exposure and temperature required for the bulk-phase oxidation are determined by the nature and reactivity of the metal. Thus, an O_2 exposure of 2 L is sufficient for the formation of a ~ 10 Å cerium oxide film at room temperature[84] (Fig. 11). The first oxidised layer on titanium, magnesium, aluminium, and chromium becomes protective and prevents the formation of the bulk-phase oxide[84,293]. A kinetic study of the oxidation of iron[295] showed that the oxidation process proceeds in two stages—rapid oxidation with formation of four oxide layers, and a slow stage with formation of ten atomic oxide layers. Evidently studies in this field are extremely informative. Table 3 gives a brief compilation of the results of studies on the adsorption of other inorganic molecules: CO_2, NO_2, N_2, H_2O, and H_2.

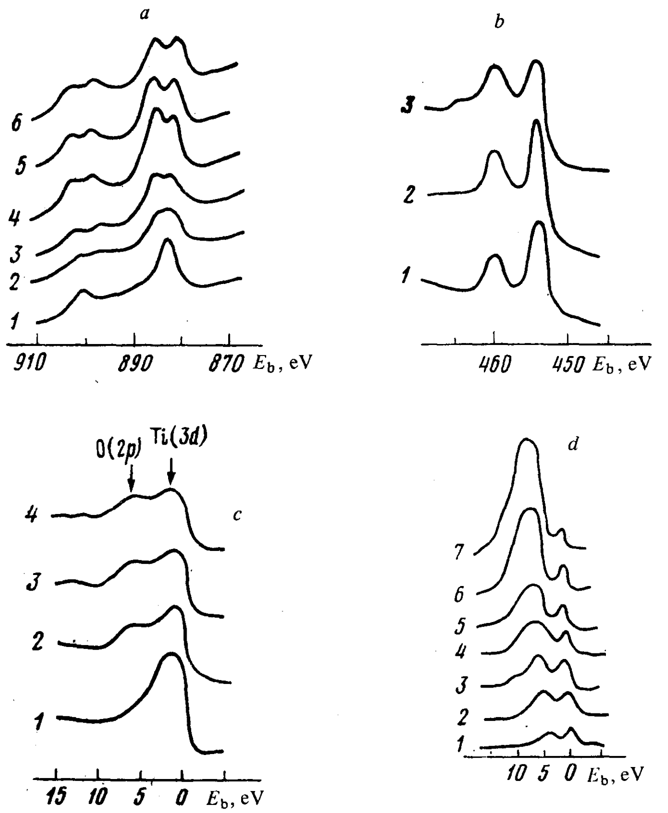


Figure 11. Adsorption of O_2 and surface oxidation of metals[84]: a) adsorption of O_2 on cerium, Ce(3d) lines [1) 0L; 2) 2L; 3) 10L; 4) 40L; 5) 100L; 6) 1000L]; b) adsorption of O_2 on titanium, Ti(2p) lines [1) 0L; 2) 1000L; 3) 3000L]; c) adsorption of O_2 on titanium, XPE spectra of the (Al $K\alpha$) valence band [1) 0L; 2) 300L; 3) 1000L; 4) 3000L]; d) adsorption of O_2 on titanium, UPE spectra, He(II) [1) 0L; 2) 1L; 3) 3L; 4) 10L; 5) 30L; 6) 100L; 7) 300L].

Until recently the number of PES studies dealing with the adsorption of hydrocarbons on metals was very limited. This was due to the experimental difficulties and the difficulties in the interpretation of the spectra. At the same time, this application of the method is of significant interest for organic catalysis. Studies which yielded extremely interesting data about the nature of the chemical bond between a number of hydrocarbons and metal surfaces have been carried out recently.

Table 3. Results of the study of the adsorption of certain inorganic molecules on metals.

Adsorbate	Adsorbent	Principal results	References
CO_2	Mo	the reaction CO_2 (gas) $\rightarrow CO_{ads} + O_{ads} \rightarrow C_{ads} + O_{ads}$ observed in the temperature range 77–298 K	240
CO_2	Au	monolayer and multilayer adsorption observed at 77 K	244
CO_2	Ni	reversible adsorption observed	262
CO_2	Pt	physical adsorption observed at 77 K	243,245
N_2	W	γ-state (weakly ads.) $\xrightarrow{300\ K}$ β-form (strongly ads.) transition observed	278
N_2	W (100)	two states of nitrogen observed	301,302
N_2	Ni	molecular adsorption found at 80 K	262,292
N_2	Fe (100)	two states of nitrogen found at 298 K	303,304
NO_2	Ni	molecular and dissociative adsorption found (77–400 K)	292,303 277
NO_2	Fe	dissociative adsorption observed at 298 K	292,303
N_2O	Ni	multilayer condensation with subsequent dissociation of N_2O observed at 80 K	
H_2O	Mo, Au	molecular and dissociative adsorption found	238,240
H_2O	Pt	molecular adsorption observed at 160 K	281
H_2O	Mg	formation of OH groups at 77 K followed by formation of MgO found	298
H_2O	Al, Cr, Mn	conditions for the formation of oxides and hydroxides investigated	298
H_2O	r.e.	the formation of oxides and hydroxides observed	299
H_2*	W	two adsorption states found on the (100) and (110) faces	302,305

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*The adsorption of H_2 was also investigated on Ir(100)[268], Pd(110)[256], Ni(111)[306], Fe, Cu[266], and Ti[307].

One of the first studies dealt with the condensation and adsorption of ethylene, acetylene, and benzene on nickel [(111) face of a single crystal] and it was shown[31,308] that E_b and the intensity of the peak of the valence σ orbital depend on the type of hybridisation of carbon atoms and are consistent with LCAO-MO SCF calculations. Physical adsorption entails a relaxation shift of the σ and π orbitals relative to E_b in the gas phase. In chemisorption the energies of the π orbitals approach those of σ-orbitals, which indicates the formation of a πd-bond at right angles to the surface; there is no rehybridisation of the σ-bond. Data for C_2H_4/Ni have been used[309] to calculate the structure of the adsorption complex. It has been shown by the method of $X\alpha$-scattered waves that UPES data support the formation of a π-complex of ethylene adsorbed on two nickel atoms, the Ni–Ni bond being perpendicular to the plane of the molecule. It has been noted that UPES data do not make it possible to distinguish this structure from that of the σ-complex in which the Ni–Ni bond is parallel to the C_2H_4 plane. The latter complex may be intermediate in the catalytic process in view of the weaker C–C bond. We may note that the model proposed cannot be regarded as rigorously proved because of the assumptions made in calculations and in the separation of chemical and relaxation shifts.

In studies on the adsorption of ethylene and acetylene on copper and iron[266,310] no correlation was observed between the heats of adsorption and the shifts of the signals due to the π-levels. The importance of taking into account the interaction within the adsorption layer was pointed out in an investigation of the adsorption of ethylene on Pt (100), although it is not clear how this is reflected in the spectra[247]. Interesting results were obtained in a study of the interaction of ethylene and acetylene with the Ir(100) and α-Fe(100) surfaces by a combined method: LEED, UPES, and Auger spectroscopy[311,312]. According to the changes in the spectra, the formation of a πd-bond ("back-donation") is accompanied by perturbation of low-lying σ-orbitals, which are not directly involved in the bond. Such perturbation results in distortion (extension and twisting) of the bonds in the chemisorbed molecules, with subsequent bond dissociation and formation of fragments (Fig. 12). Depending on the reactivity of the metals and on the state of the surface (clean, carbon-coated, oxidised) the fragmentation process can occur at different temperatures. Thus, no distortion in the structure of the C_2H_2 molecule was observed on nickel and copper, on Ir(100) the acetylene molecule is stretched and twisted at 298 K[311], while on α-iron at 123 K it fragments with formation of CH_n (n = 1 or 2) radicals and possibly $CCH_2^{\cdot}$.[312] The bond distortion effect in C_2H_2 diminishes on passing from the clean to the carbon-coated surface and is scarcely observed on the oxidised surface[312]. C_2H_4 behaves significantly differently: on α-iron the molecule fragments with formation of $CH_2^{\cdot}$ (Fig. 12). This hypothesis is supported by data for the adsorption of H_2 on the carbon-coated surface of α-iron (Fig. 12); the spectra are close to the corresponding C_2H_4 spectra. In contrast to α-iron, on iridium and nickel at $T < 300$ K, ethylene undergoes preferential dehydrogenation with formation of acetylene[308,312] (Fig. 12). At a higher temperature (600° C) a spectral band characteristic of the σ-band of pyrolytic graphite arises in the Ni(100) spectrum, which indicates the cracking of C_2H_4.[313] The mechanism of the formation of carbon on the W(100) surface in the decomposition of butadiene at 1000 K has been investigated[301].

When halogenoalkenes interact with the Pt(100) and Pt(111) surfaces, both dissociative adsorption (vinyl fluoride and chloride), accompanied by the elimination of the halogen, and non-dissociative adsorption ($CH \equiv C-CF_3$, $CH_2=CH-CF_3$, CF_2CFCl) are observed[314,315]. The degree of dissociation of vinyl fluoride, determined from the ratio $I[F(1s)]/I[C(1/s)]$ depends on the crystal face index [80% for the (111) face and 40% for the (100) face] and is inhibited in the presence of CO on the surface. The adsorption and decomposition of methanol and formaldehyde on tungsten[316] and palladium[317] and of CH_3OCH_3, $(CH_3)CHO$ and $(CH_3)_2CO$ on palladium[317] were investigated. On tungsten, for coverages corresponding to saturation, methanol and formaldehyde form molecular complexes and at low coverages the β-CO state arises already in the early stages of adsorption[316]. At 120 K on palladium, the bond between the adsorption complex and the surface is formed via an atomic orbital of oxygen, which has a lone electron pair, while at 300 K the decomposition of the molecules begins and chemisorbed CO appears. The d-band of palladium is involved in the formation of the bond, which entails a decrease in the intensity of the spectrum on adsorption. Using the chemical shifts, an attempt was made to estimate the strength of the adsorbate–adsorbent interaction and E for the chemisorption bond within the framework of Mulliken's theory of donor–acceptor complexes[317]. Catalytic decomposition of HCOOH on copper, nickel, and gold, at 80–295 K leads to a change in the UPE spectra and a shift of the 1s level of O by 2 eV, which is associated with the formation of a formate ion[318]. With increase of temperature, the formate ion decomposes and the H_2 and CO_2 formed are desorbed into the gas phase. The activation energies found from these data are close to those obtained in the catalytic experiment. Comparison of the catalytic activities in the sequence Au < Fe < Ag < Ni < Cu < Pt in the decomposition of HCOOH and the densities of states in the vicinity of the Fermi level in these metals led to the conclusion that there is no correlation between the above quantities[37,318].

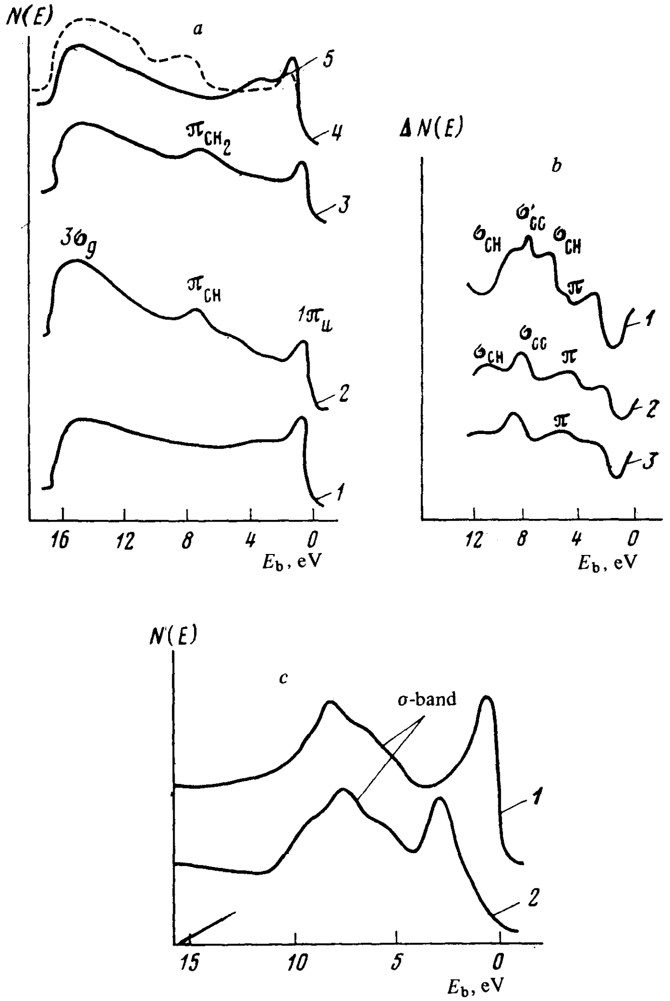

Figure 12. Adsorption of ethylene and acetylene on metals: *a*) C_2H_2, C_2H_4, and H_2 on α-Fe(100)[312], UPE spectra, He(I) [1) clean surface; 2) 123 K, C_2H_2 (6*L*); 3) 123 K, C_2H_4 (6*L*); 4) carbon-coated surface of α-Fe(100); 5) adsorption of H_2 on the carbon-coated surface of α-Fe(100)]; *b*) adsorption of C_2H_4 on nickel, differential He(I) spectra[308] [1) C_2H_4 1.2*L*, 100 K; 2) C_2H_4 1.2*L*, heating to 300 K; 3) C_2H_2 1.2*L* (100–300 K)]; *c*) high-temperature adsorption of C_2H_4 on Ni(110), He(II) UPE spectra[313] [1) C_2H_4, 780*L*, 873 K, $C_2H_4 \rightarrow 2H_2 + 2C$(graphite); 2) spectrum of pyrolytic graphite cleaved *in vacuo*] [*N*(*E*) is the intensity and Δ*N*(*E*) the differential intensity].

Of the other studies which have been made, we shall mention the investigation of the layer-by-layer condensation of CB_4 [246] and the chemisorption of C_2N_2 on platinum[319]. In the latter case interaction with transfer of a *d* electron of the metal to the unoccupied $2\pi^*$ orbital of the adsorbate was postulated. There are data for the adsorption of NH_3 on W(100),[320] of iodoaniline on gold[321], and of H_2S and SO_2 on nickel[259,282].

The spectra of C_2H_6, C_6H_6, CH_3OH, C_2H_5OH, H_2CO, H_2O, and NH_3 in the gaseous state and condensed at 77 K on MoS_2 [322] confirm the hypothesis that the relaxation shifts are equivalent in different systems. In general, the same conclusion may be arrived at by examining the physical adsorption of Xe on W(111)[274] and nickel[323], for which the spectra of the inner and valence levels exhibit identical shifts relative to the gas phase (1.1–1.3 eV for nickel). However, in a study of the excited HeI line in the spectrum of the 5*p* level of Xe on the (100) face of tungsten[324] a marked broadening of the signal due to the $5p_{3/2}$ sublevel was observed and interpreted as a consequence of the splitting of the $5p_{3/2}$ xenon sublevel under the influence of the crystal field. Thus even in physical adsorption the system of adsorbate levels may undergo non-identical perturbations.

(b) Catalytic reactions on metal surfaces. The methods for the measurement of XPE and UPE spectra make it possible to investigate surface reactions under two sets of conditions: (1) with the reaction mixture passed over the catalyst and scanning of the spectra. Since the pressure of the reactants is very low ($< 10^{-7}$ mmHg), coverages sufficient for the recording of the spectra (approximately 0.05 of a monolayer) cannot always be attained; (2) reactions in the adsorption layer; in this case it is possible to achieve a higher surface concentration of one of the components. Evidently the interactions of many adsorbates with the surface, leading to a chemical alteration of the adsorbate (for example, the decomposition of NO and CH_3OH, the dehydrogenation of C_2H_4, etc.) can be regarded as reactions in the adsorption layer. However, mainly qualitative data concerning the structures of the adsorption complexes were obtained in the studies quoted above. Furthermore, there have been investigations where the reaction kinetics were studied by PES, and definite conclusions about the reaction mechanisms were reached. This applies to the investigations of reactions of molecular hydrogen with molecular oxygen[281,325,326], of carbon monoxide with molecular oxygen[253,259,264,327,328], of carbon monoxide with molecular hydrogen and nitric oxide[256,329], and of hydrogen sulphide with molecular oxygen[265].

The first attempt to investigate the reaction of H_2 with $O_{2(ads)}$/Pt directly during the scanning of the XPE spectra was apparently made in Norton's study[281]. After the adsorption of oxygen at 120 K $\{E_b[O(1s)] = 530.2$ eV$\}$, a stream of H_2 (10^{-7} mmHg) was passed through the system and the specimen was subjected to linear heating. An O(1*s*) peak with $E_b = 533$ eV (evidently $H_2O_{(ads)}$) appeared at 140 K, indicating the onset of the reaction, which terminated at 150 K. The line with $E_b = 533$ eV disappeared at 170 K and water was desorbed. The kinetics of this reaction were studied and an equation describing the reduction of $O_{2(ads)}$ was derived. In contrast to this reaction, the oxidation of adsorbed H_2 was much slower, which was explained by the poisoning of the active centres by hydrogen. According to some results[325,326] the probability of the interaction of an H_2 molecule with an $O_{2(ads)}$ molecule, leading to reaction at $\theta = 0.5$ at room temperature on platinum, is approximately 0.7, which is ten times greater than the value found by Norton. The authors[325,326] believe that this discrepancy is caused by the inaccuracy of the measurement of pressure in Norton's study[281].

The adsorption of CO on the Ru(001) surface covered by oxygen entails a change in the O(1*s*) lines, indicating the joint adsorption of CO and O_2 and then a displacement of O_2 from the surface (15–20% of the initial coverage[257]). It is suggested that part of the CO reacts with O_2 even at low temperatures. The oxidation of CO on Ir(111) was studied directly during the recording of the spectra[328]. The results obtained with the aid of XPES show that the reaction proceeds via the Langmuir–Hinshelwood mechanism. According to data obtained with the aid of LEED, flash desorption, and UPE spectroscopy, the oxidation of carbon monoxide on Ir(111) can proceed via the Eley–Rideal mechanism[264].

The interaction of carbon monoxide with molecular hydrogen on the Ni(111) surface was studied at relatively low temperatures (< 400 K). According to LEED data, a (2×2) structure of the adsorbate is produced[323], although the interaction of CO with H_2 is still insignificant and does not lead to a change in the energy of the valence orbitals. At low coverages, H_2 is present in the β_1-state, passing to the β_2-state as the degree of coverage increases. The formation of reaction complexes on the surface and of the products in the gas phase was not observed under these conditions. The interaction of H_2S with O_2 adsorbed on lead is a typical instance of a surface reaction leading to a change in the state of the elements of the support[265]. The observed changes in the positions and intensities of the O(1*s*) and S(2*p*) lines constitute the basis for the hypothesis that the reaction $PbO_{surf} + H_2{}_{gas} \rightarrow PbS_{solid} + H_2O_{gas}$ takes place.

(c) Other adsorbents. The interaction of oxygen with the basal and prismatic faces of graphite was begun by Thomas and coworkers[330,331]. In the study of catalysts having semiconducting or insulating properties certain difficulties are encountered due to the charging of the surface, the possibility of a more ready modification of the properties of the surface under the influence of radiation compared with metals, etc. One can only mention one of the first attempts to study adsorption on clean catalyst surfaces. Almy et al.[332] obtained the spectra of partly dehydrated α-Al_2O_3 (0001) and of the surface after the adsorption of H_2O, excited with the aid of He(I) lines. The specimen was subjected to preliminary cleaning in O_2 and, according to Auger spectroscopic data, its surface was free from impurities. There is an appreciable difference between the spectra of the clean surface and the surface coated by H_2O. Calculation by the method of X_α-scattered waves agreed satisfactorily with the experimental spectrum. A cluster model was chosen, according to which H_2O molecules are strongly bound to the α-Al_2O_3 surface. The number of UPE studies on powdered non-conducting specimens has been extremely limited[118,156]. Studies by the XPES method, but not under "clean surface" conditions, were examined above.

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The studies carried out hitherto demonstrate the high efficiency of the PES method in the study of catalytic and adsorption problems. The method makes it possible to obtain unique information about the structures of the surface layers of catalysts and about the nature of adsorption complexes. There is no doubt that, as the theory of the method is developed further and experimental technique is improved, the range of problems soluble by PES in this field will be extended. The wide-scale application of PES in the study of catalytic problems will assist in deepening our knowledge about the nature of the catalytic activity of solids.

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Methods of Mathematical Treatment of the Results of Physicochemical Studies on Complex Compounds

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The general principles of the determination of the equilibrium constants and the physicochemical parameters of complexes under the conditions of their dissociation are examined. The possibilities of approximate computational methods and direct analytical procedures for the solution of systems of the corresponding equations are analysed. Various methods involving the simultaneous determination of the equilibrium constants and physicochemical parameters of complexes, based on the statistical principle of maximum probability, are compared. The ways of the most rational employment of computer techniques in the study of involved complex-formation reactions by various physical methods are discussed.
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I. INTRODUCTION

The problem of coordination interaction has been attracting much attention by investigators working in different fields because this type of intermolecular interaction plays a major role in many physical, chemical, and biological phenomena. The range of energies of coordination interactions is extremely wide, starting with the formation of weak self-associated species in liquids and vapours and extending as far as the formation of fairly stable complexes (various molecular complexes, hydrogen-bonded complexes, complexes of ions with various ligands, etc.).

The advances made in recent years in the study of the nature of the coordinate bond and the characteristics of the formation and the properties of complex compounds have been to a large extent due not only to the employment of modern physical research methods but also to improvement of the mathematical procedures used in the interpretation of the experimental results[1-11]. Many physical research methods such as spectrophotometry, NMR, measurements of dipole moments, calorimetry, etc. require that the experiment be carried out in the liquid phase, in solution, or in the vapour phase, i.e. under conditions where there is a possibility of the dissociation of the complexes into the initial components. Any measured property of the solution or vapour is then an overall characteristic of the equilibrium mixture of the initial components and the complexes formed in the system. In order to determine particular parameters of the complexes, it is necessary to know the composition of the equilibrium mixture and hence the stability constants of the complexes. The latter can be determined in an individual experiment, for example, by measuring the colligative properties of the solutions, i.e. properties which depend only on the concentrations of the components of the equilibrium mixture and are independent of the physical characteristics of these molecules. However, even when the equilibrium constants for multistage complex-formation reactions are known, the calculation of equilibrium concentrations is an extremely complex task, since it requires the simultaneous solution of a system of non-linear equations corresponding to the Law of Mass Action and the material balance equations.

The development of a mathematical description of the chemistry of equilibrium processes leads to the possibility of determining the equilibrium constants and the physicochemical parameters of the complexes formed in a given experiment. Methods which permit the determination of the parameters of the complexes without isolating the latter in a pure state are of special interest. The formulation of the experiment under these conditions reduces to the measurement of a physicochemical property of the solution or vapour as a function of the overall concentration of the initial components, mixed in various molar proportions [titration and isomolar series (continuous variations) methods]. In the vast majority of cases the simultaneous determination of the physical parameters and stability constants of complexes in a single experiment is virtually impossible without the use of a computer.

Thus the realisation of the potential possibilities of even extremely informative and accurate physical methods, which require that the experiment be carried out in the liquid or gas phases, depends to a large extent on the reliability of the method of mathematical treatment of the results of the measurements.

The first studies on these lines were carried out towards the end of the 1940s and the beginning of the 1950s, i.e. at a time when computer technology had not developed sufficiently. Different versions of analytical and graphical extrapolations based on approximate equations were widely used. It is noteworthy that, in the analysis of data obtained by these methods, no account is frequently taken of the degree of approximation of the equations employed and attempts are actually made to solve approximate equations by means of a computer. Clearly such a procedure cannot be regarded as rational. Further development of computer technology led to a rigorous solution of the problem under consideration.

In this review an attempt is made to analyse the present state of methods for the mathematical treatment of the results of physicochemical studies of complex formation reactions, to demonstrate the advantages and disadvantages of many computational methods used, and to discover the most rational ways of employing computers for a rigorous solution of the problem of the simultaneous determination of the equilibrium constants and physical parameters of complexes.

II. GENERAL PRINCIPLES OF THE DETERMINATION OF THE PARAMETERS OF DISSOCIATING COMPLEXES

The methods for the treatment of the results of physicochemical experiments designed to determine the parameters of complexes are based on the following relations: (1) the equation relating the measured property of the solution to the parameters of the components of the equilibrium mixture and their concentrations; (2) the Law of Mass Action equation; (3) the material balance equation.

An experimentally measured physicochemical property of a system containing an equilibrium mixture of the initial components and the complexes formed is a function of the parameters of all the components of the mixture and their equilibrium concentrations. The measured property X can be represented by the following additive function with a degree of approximation which is adequate for many methods[12]:

$$X = X_z + L\left(x_A C_A + x_B C_B + \ldots + \sum_{i=1}^{n} x_i C_i\right), \qquad (II.1)$$

where x_A, x_B, ..., x_i are the parameters of the initial compounds A, B, ..., and the ith complex respectively, c_A, c_B, ..., c_i are their equilibrium molar concentrations, n is the number of complexes in the mixture, L is a constant whose magnitude and dimensions depend on the physical method used and the experimental conditions, and X_Z is the corresponding property of the medium (solvent).

For example, in spectrophotometry the measured property of the solution is the optical density D at a given wavelength λ. Eqn. (II.1) then assumes the form of Eqn. (II.2). In order to synthesise the formulation of this and subsequent equations, we shall assume that the system contains only two initial components A and B:

$$D = l\left(\varepsilon_A C_A + \varepsilon_B C_B + \sum_{i=1}^{n} \varepsilon_i C_i\right) + D_z, \qquad (II.2)$$

where l is the optical pathlength, ϵ_A, ϵ_B, and ϵ_i are the molar extinction coefficients of A, B, and the ith complex, and D_Z is the optical density of the solvent.

In the determination of the dipole moments of complexes by the Debye method the measured dielectric constants ϵ and the densities d of the solution may be represented by the following functions[12]:

$$\begin{aligned} \varepsilon &= \alpha_A C_A + \alpha_B C_B + \sum_{i=1}^{n} \alpha_i C_i + \varepsilon_z, \\ d &= \gamma_A C_A + \gamma_B C_B + \sum_{i=1}^{n} \gamma_i C_i + d_z, \end{aligned} \qquad (II.3)$$

where α_A, α_B, α_i and γ_A, γ_B, and γ_i are parameters linked to the dipole moments of the corresponding molecules by the expressions

$$P_{i,\infty} = \frac{\varepsilon_S - 1}{\varepsilon_S + 1} \cdot \frac{1}{d_S}\left(M_i - 1000\gamma_i + \frac{3000}{(\varepsilon_S + 2)^2}\alpha_i\right)$$

$$\mu_i = 0.01283\sqrt{(P_{i,\infty} - P_A - P_E)\,T} \quad .$$

Here $P_{i,\infty}$ is the molar polarisation of the substance at infinite dilution, P_A, and P_E are the atomic and electronic polarisations (it is usually assumed that $P_A + P_E = R_i$, R_i being the molar refraction of the substance for the sodium D line), and T is the absolute temperature.

In high-resolution NMR spectroscopy (under the conditions of rapid exchange) one usually measures the chemical shift of the averaged signal δ, whose position depends on the contributions of all the components of the equilibrium mixture containing the resonating nucleus. If the molecules of A and B incorporate respectively y and z atoms with the resonating nucleus, then Eqn. (II.1) becomes[13,14]

$$\delta = \frac{1}{yC_{A_0} + zC_{B_0}}\left(y\delta_A C_A + z\delta_B C_B + \sum_{i=1}^{n} \delta_i C_i\right), \qquad (II.4)$$

where δ_A, δ_B, and δ_i are the chemical shifts of the signals due to the nuclei in the corresponding molecules.

In calorimetric measurements the amount of heat Q evolved as a result of the complex formation reaction is related to the enthalpies of formation ΔH_i of the complexes from the components as follows[6-10]:

$$Q = v\sum_{i=1}^{n} \Delta H_i C_i, \qquad (II.5)$$

where v is the volume of the solution (litres). It is readily seen that Eqn. (II.5) is also a special case of Eqn. (II.1) in which $x_A = x_B = 0$, $x_i = \Delta H_i$, $L = v$, and $X_Z = 0$.

The quantities x_A, x_B, and some of the x_i may be zero not only in calorimetric measurements but also in studies by other physicochemical methods. For example, in spectrophotometry zero values are assumed by the parameters of those substances which have no absorption bands in the experimental frequency range; in NMR spectroscopy the characteristics of the molecules without resonating nuclei are zero.

Methods based on the measurement of colligative properties of the system are used frequently to determine the equilibrium constants. These properties are independent of the physical parameters of the molecules present in the equilibrium mixture, which makes it possible to assume that $x_A = x_B = x_i = \ldots = x_n = 1$. In this case Eqn. (II.1) becomes

$$X = L\left(C_A + C_B + \sum_{i=1}^{n} C_i\right) + X_z. \qquad (II.6)$$

This simplified form of the general equation (II.1) may be used to interpret data obtained by cryoscopic, ebullioscopic, tensimetric, gas–liquid chromatographic, etc. methods.

The concentrations of the components of the equilibrium mixture are related to the equilibrium constants of the complex formation reactions by the Law of Mass Action equations. Assuming that the test solutions or the gas mixture are ideal (the activity or fugacity coefficients are unity), the equilibrium constant of the reaction

$$pA + qB \overset{K}{\rightleftarrows} A_pB_q, \qquad (II.7)$$

can be formulated in the following form:

$$K = [A_pB_q]/[A]^p \cdot [B]^q \, . \qquad (II.8)$$

If the assumption of ideality is invalid, the concentrations in Eqn. (II.8) must be replaced by the activities. K depends on the way in which the concentration is expressed. At concentrations expressed on the molar scale, Eqn. (II.8) becomes

$$K=\frac{C_{A_pB_q}}{(C_A)^p\,(C_B)^q}\quad\text{or}\quad C_{A_pB_q}=K\,(C_A)^p\,(C_B)^q\,. \tag{II.9}$$

The complex A_pB_q with $p > 1$ and(or) $q > 1$ is as a rule formed in stages. The equilibrium mixture can then contain complexes having different compositions. Furthermore if the initial molecules A and B show a tendency towards self-association, then the mixture may contain also associated species of the type A_m and B_n.[9] The stepwise formation of the complex AB_n can be represented schematically thus:

$$\begin{gathered}A+B\overset{K_1}{\rightleftarrows}AB,\ C_1=K_1C_AC_B;\\ AB+B\overset{K_2}{\rightleftarrows}AB_2,\ C_2=K_2C_1C_B=K_1K_2C_AC_B^2;\\ \cdots\cdots\cdots\cdots\cdots\cdots\\ AB_{n-1}+B\overset{K_n}{\rightleftarrows}AB_n,\ C_n=K_nC_{n-1}C_B=K_1K_2\,\ldots\,K_nC_AC_B^n.\end{gathered} \tag{II.10}$$

The mechanism of the same reaction can be formulated as follows:

$$\begin{gathered}A+B\overset{\beta_1}{\rightleftarrows}AB,\ C_1=\beta_1C_AC_B;\\ A+2B\overset{\beta_2}{\rightleftarrows}AB_2,\ C_2=\beta_2C_AC_B^2;\\ \cdots\cdots\cdots\cdots\\ A+nB\overset{\beta_n}{\rightleftarrows}AB_n\ C_n=\beta_nC_AC_B^n\ .\end{gathered} \tag{II.11}$$

Thus we have for the stepwise formation of complexes AB_i

$$c_i=K_iC_{i-1}C_B=K_1K_2\,\ldots\,K_ic_Ac_B^i=\beta_i\,c_A\,c_B^i, \tag{II.12}$$

where $\beta_i=\prod_{l=1}^{i}K_l$ is the overall stability constant of the complex AB_i.

The mechanism of the involved reaction whereby the complex A_mB_n is formed can be formulated, for example, as follows when account is taken of the self-association of component A:

$$\begin{gathered}A+A\overset{K_1}{\rightleftarrows}A_2,\ C_1=K_1C_A^2;\\ A+B\overset{K_2}{\rightleftarrows}AB,\ C_2=K_2C_AC_B;\\ AB+A\overset{K_3}{\rightleftarrows}A_2B,\ C_3=K_3C_AC_2=K_2K_3C_A^2C_B;\\ AB+B\overset{K_4}{\rightleftarrows}AB_2,\ C_4=K_4C_2C_B=K_2K_4C_AC_B^2;\\ AB_2+A\overset{K_5}{\rightleftarrows}A_2B_2,\ C_5=K_5C_4C_B=K_2K_4K_5C_A^2C_B^2;\\ A_2B_2+B\overset{K_6}{\rightleftarrows}A_2B_3,\quad C_6=K_{65}C_5C_B=K_2K_4K_5K_6C_A^2C_B^3.\\ \cdots\cdots\cdots\cdots\cdots\cdots\end{gathered}$$

In the general case the equilibrium concentration of the complex formed in the ith stage of any involved reaction is a function of the equilibrium constant of the ith and preceding reaction stages and the equilibrium concentrations of the corresponding complexes in the mixture:

$$C_i=f_i\,(C_A,\ C_B,\ \ldots,\ C_1,\ \ldots,\ C_{i-1},\ K_i)=\varphi_i\,(C_A,\ C_B,\ \ldots,\ K_1,\ \ldots,\ K_i). \tag{II.13}$$

The form of the functions f_i and φ_i depends on the stoichiometry of the reaction investigated.

The most general and convenient method of representing the mechanisms of involved chemical reactions is based on their formulation with the aid of numerical matrices of stoichiometric coefficients. The most general method of such formulation has been proposed by Temkin[15] and Aris[16]. The equation for the ith stage of the reaction

$$pA+qB+\ldots\rightleftarrows p'E+q'D+\ldots$$

can be formulated in the following way by transferring all the terms to the left-hand side:

$$\sum_{l=1}^{m+s}\alpha_{il}A_l=0,\ i=1,2,\ \ldots,\ n,$$

where m is the number of reaction products, s the number of reactants, n the number of stages, and α_{il} the stoichiometric coefficient of the component A_l in the ith reaction stage, which can be any integer (positive, negative, or zero).

The stoichiometric mechanism of an n-stage reaction is a matrix of integers:

$$\|\alpha_{il}\|;\ i=1,\ \ldots,\ n;\ l=1,\ \ldots,\ m+s. \tag{II.14}$$

The number of columns in this matrix is equal to the number of all the substances involved in the reaction and the number of rows is equal to the number of reaction stages. If any of the reaction components does not participate in the ith stage, the corresponding element in the ith row of the matrix (II.14) is assumed equal to zero. A matrix of type (II.14) is used in the interpretation of data on the kinetics of involved chemical reactions[17-19].

An abbreviated version of the matrix (II.14) rather than the matrix itself is usually employed for complex formation reactions. If each reaction stage is formulated in terms of the dissociation of the complex into its components:

$$A_{p_i}B_{q_i}D_{r_i}\ \ldots\ \overset{\beta_i}{\rightleftarrows}p_iA+q_iB+r_iD+\ \ldots,$$

then part of the matrix (II.14), which is made up of the stoichiometric coefficients of the complexes, will always be an $n\times n$ unit matrix. Tobias and coworkers[20] and Sillén and coworkers[21-23] do not write out this unit matrix and formulate the reaction scheme solely in terms of the matrix of the stoichiometric coefficients of the initial components A, B, D, ...:

$$\|p_iq_ir_i\ \ldots\ \|=\|p_{il}\|\ i=1,\ \ldots,\ n;\ l=1,\ \ldots,\ s. \tag{II.15}$$

A matrix of type (II.15) has been widely used in calculations of the equilibria of involved complex-formation reactions in two-component[24-29] and multicomponent[30-42] systems.

The matrix (II.15) makes it possible to formulate the equation of the Law of Mass Action in a general form[20-23]:

$$c_i=\beta_i\,(C_A)^{p_i}(C_B)^{q_i}(C_D)^{r_i}\ \ldots\ . \tag{II.16}$$

We may note that the formulation of stoichiometric schemes for involved complex-formation reactions in terms of matrices of type (II.15) makes it possible to calculate only the overall equilibrium constants β_1, β_2, ..., β_n corresponding to, for example, scheme (II.10). Another method of the matrix formulation of a stoichiometric scheme for a multistage reaction has been proposed[13,43]. It permits the determination of both the overall equilibrium constants and the constants for each stage. It is assumed that each reaction stage involves the formation of a single complex from two reactants:

$$m_{i1}D_{m_{i2}}+m_{i3}D_{m_{i4}}\overset{K_i}{\rightleftarrows}m_{i5}D\,m_{i6}, \tag{II.17}$$

where m_{i1}, m_{i3}, and m_{i5} are the stoichiometric coefficients of the ith reaction, m_{i2}, m_{i4}, and m_{i6} are the numbers of substances D participating in the given stage, which may be the components A, B, ... and the complexes formed in preceding stages. The substances are numbered as follows: the numbers 1, 2, ..., s are assigned to the initial components A, B, ... and the numbers $i+s$ are assigned to the complexes formed in the ith stage. The scheme for an ***n***-stage reaction is formulated by means of a matrix of the following form:

$$M = \| m_{i1} m_{i2} m_{i3} m_{i4} m_{i5} m_{i6} \|,\ i = 1,\ \dots,\ n, \qquad \text{(II.18)}$$

where the number of rows is equal to the number of reaction stages and the number of columns is six.

The equation of the Law of Mass Action can be written in the following form using the elements of the matrix (II.18):

$$C_i = C_{m_{i6}} = [K_i (C_{m_{i2}})^{m_{i1}} (Cm_{i4})^{m_{i3}}]^{1/m_{i5}}, \qquad \text{(II.19)}$$

where C_{mi_2}, C_{mi_4}, and C_{mi_6} are the equilibrium concentrations of the corresponding substances.

It is noteworthy that, when matrices of types (II.15) and (II.18) are used, a stoichiometric reaction scheme can be usefully set up in such a way that the complex of the given composition is formed solely in one reaction stage. This makes it possible to obtain a system of independent Law of Mass Action equations[15-19].

For a complex formation reaction with participation of s initial components A, B, ..., one can formulate s material balance equations with respect to each component separately:

$$\begin{aligned} C_{A_0} &= C_A + \sum_{i=1}^{n} p_i C_i, \\ C_{B_0} &= C_B + \sum_{i=1}^{n} q_i C_i\ , \end{aligned} \qquad \text{(II.20)}$$

where C_{A_0} and C_{B_0} are the overall concentrations of substances A, B, ... Equations for the calculation of p_i and q_i from the matrix (II.18) have been published[13,43].

Simultaneous solution of Eqns. (II.1), (II.13), and (II.20) permits the simultaneous calculation of the stability constants K_1, ..., K_n of the complexes formed and the required parameters x_1, ..., x_n.

If the reaction investigated has n stages and s initial components are involved in the interaction, then one can write $n + s + 1$ equations for each jth experiment and the total number of equations for N experiments is $N(n + s + 1)$. The unknowns which must be determined using the above system of equations are as follows: C_A, C_B, ...; C_1, ..., C_n; K_1, ..., K_n; x_1, ..., x_n. The total number of unknowns is $(n + s)N + 2n$. By comparing the number of equations with the number of unknowns, it is easy to determine the minimum number of experiments N necessary to solve the problem formulated:

$$N \geqslant 2n. \qquad \text{(II.21)}$$

Thus even the study of complex-formation reactions with not unduly complicated stoichiometric ($n \geqslant 2$) necessitates the solution of a system of non-linear equations with a fairly large number of unknowns.

There exist various approaches to the solution of the problem of the determination of the parameters of the complexes from the results of a physicochemical experiment. In terms of mathematical procedures, they can be divided into three groups.

1. Approximate methods involving linear graphical extrapolation or a simplified analytical calculation.
2. Methods based on the exact solution of the system of equations.
3. Methods involving the search for the parameters on the basis of the statistical principle of maximum probability.

These methods of calculation will be discussed below.

Any physicochemical method permitting the determination of equilibrium constants over a temperature range can be used to determine the thermodynamic parameters of the complex formation process: $\Delta G°$, $\Delta H°$, and $\Delta S°$. The free energy $\Delta G°$, enthalpy $\Delta H°$, and entropy $\Delta S°$ of a given reaction under standard conditions are related to the equilibrium constants K as follows:

$$\Delta G^0 = -RT \ln K = \Delta H^0 - T\Delta S^0. \qquad \text{(II.22)}$$

$\Delta H°$ and $\Delta S°$ are usually calculated from the relation between $\ln K$ and $1/T$ as the linear coefficients of Eqn. (II.22) written in the following form[2,5,6,44,45]:

$$\ln K = -\Delta H^0/RT + \Delta S^0/R. \qquad \text{(II.23)}$$

In principle it is not obligatory to calculate initially the equilibrium constants for each given temperature and then evaluate $\Delta H°$ and $\Delta S°$ from Eqn. (II.23).[46] As suggested by the present authors[47], $\Delta H°$ and $\Delta S°$ may be adopted as the required parameters and Eqns. (II.1), (II.13), (II.20), and (III.23) may be solved simultaneously.

In order to determine the enthalpies and entropies of formation of complexes from the temperature variation of the equilibrium constants, one usually begins with the hypothesis that $\Delta H°$ and $\Delta S°$ are independent of temperature. This assumption is more or less valid when $\Delta H°$ and $\Delta S°$ are determined from data obtained over a comparatively narrow temperature range and close to standard conditions[48]. However, in studies over a wide temperature range, where the heat capacity of the system may change significantly, one must take into account the possible temperature dependence of $\Delta H°$ and $\Delta S°$.[49-51] This applies particularly to tensimetric measurements, which are carried out, as a rule, at a high temperature (200° to 600°C) over a range of the order of 100-200 K.[51-53] The values of ΔH°_{T} and ΔS°_{T} obtained from such measurements are difficult to adjust to standard conditions owing to the lack of data for the heat capacities of the complexes.

III. APPROXIMATE METHODS FOR THE CALCULATION OF THE PARAMETERS OF COMPLEXES BASED ON A LINEAR GRAPHICAL EXTRAPOLATION

In order to simplify the solution of the system of non-linear equations (II.1), (II.13), and (II.20), one frequently uses particular approximations or limitations are imposed on the experimental conditions. This makes it possible to convert the equations into a form convenient for the graphical determination of the required parameters.

For a single-stage complex-formation reaction, where only one complex A_pB_q is formed in solution [Eqn. (II.7)], the equilibrium concentration C_C and the stability constant of the latter can be expressed[1,6] in the following form on the basis of Eqns. (II.1), (II.9), and (II.20):

$$C_c = \Delta X/\Delta x, \qquad \text{(III.1)}$$

where

$$\Delta X = X - X_z - L(x_A C_{A_0} + x_B C_{B_0}) \text{ and } \Delta x = L(x_c - p x_A - q x_B).$$

The above symbols (ΔX and Δx) will be used also in subsequent equations.

$$K = C_c/(C_{A_0} - pC_c)^p (C_{B_0} - qC_c)^q. \qquad \text{(III.2)}$$

For 1 : 1 complexes ($p = q = 1$), the following expression may be obtained on the basis of Eqns. (III.1) and (III.2):[6]

$$\frac{1}{K} = \frac{C_{A_0}C_{B_0}}{\Delta X}\Delta x - (C_{A_0} + C_{B_0}) + \frac{\Delta X}{\Delta x}. \qquad \text{(III.3)}$$

For highly dissociated complexes, where $C_C = \Delta X/\Delta x \ll (C_{A_0} + C_{B_0})$, the last term in Eqn. (III.3) may be neglected, which yields

$$\frac{1}{K} = \frac{C_{A_0}C_{B_0}}{\Delta X}\Delta x - (C_{A_0} + C_{B_0}). \qquad \text{(III.4)}$$

After certain rearrangements, it is easy to obtain the following relations from the simplified Eqn. (III.4):[6]

$$C_{A_0}C_{B_0}/\Delta X = (C_{A_0} + C_{B_0})/\Delta x + 1/K\Delta x, \qquad \text{(III.5)}$$

$$C_{A_0}C_{B_0}/\Delta X (C_{A_0} + C_{B_0}) = 1/K\Delta x (C_{A_0} + C_{B_0}) + 1/\Delta x. \qquad \text{(III.6)}$$

Equations of type (III.5) and (III.6) are used widely for the graphical determination of the parameters of highly dissociated molecular complexes[1,2,5,6,54-81]. According to Eqn. (III.5), based on experimental data, the plot of $C_{A_0}C_{B_0}/\Delta x$ against $(C_{A_0} + C_{B_0})$ should be a straight line whose slope is $1/\Delta x$ and the intercept on the ordinate axis is $1/K\Delta x$ (Fig. 1). Hence it is possible to obtain the values of K and Δx and to calculate $x_C = \Delta x/L + x_A + x_B$ for known values of x_A and x_B [see Eqn. (III.1)] with $p = q = 1$. The same parameters may be obtained when the experimental data are represented by a plot of $C_{A_0}C_{B_0}/\Delta X(C_{A_0} + C_{B_0})$ against $1/(C_{A_0} + C_{B_0})$. According to Eqn. (III.6), the plot should be a straight line which makes an intercept on the ordinate axis equal to $1/\Delta x$ and has a slope equal to $1/K\Delta x$.

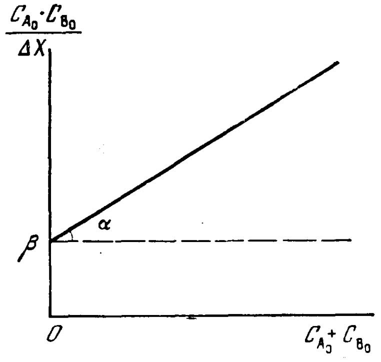

Figure 1. Determination of the parameters x_C and K from a linear plot corresponding to Eqn. (III.5); $\tan\alpha = 1/\Delta x_C$; $\beta = 1/K\Delta x_C$.

This method for the simultaneous determination of the stability contants and the physical parameters of 1 : 1 complexes was proposed for the first time by Benesi and Hildebrand[54] for the interpretation of spectrophotometric data. Apart from the condition $C_C \ll (C_{A_0} + C_{B_0})$, a further two conditions are imposed on the formulation of the experiment: firstly, there must be a large excess of one of the components, i.e. $C_{A_0} + C_{B_0} \simeq C_{B_0}$ and, secondly, the experiment must be carried out at a wavelength where only the complex absorbs. Under these conditions, one can obtain the following expression from Eqns. (III.4), (III.1), and (III.5):

$$C_{A_0}l/D = 1/K\varepsilon_C C_{B_0} + 1/\varepsilon_C. \qquad \text{(III.7)}$$

Under the same conditions, Eqns. (III.6) readily yield Scott's equation[55]:

$$C_{B_0}C_{A_0}l/D = C_{B_0}/\varepsilon_C + 1/K\varepsilon_C. \qquad \text{(III.8)}$$

Subject to the condition C_{A_0} = const., Foster and coworkers[5,56] obtain the equation

$$D/C_{B_0} = -KD + KC_{A_0}\varepsilon_C. \qquad \text{(III.9}$$

from the Benesi–Hildebrand equation. According to Eqn. (III.9), K and ϵ_C may be determined from a linear plot of D/C_{B_0} against D, whose slope is $-K$ and whose intercept on the ordinate axis is $KC_{A_0}\epsilon_C$.

Together with its various modifications, the Benesi–Hildebrand method has been used widely in the interpretation of not only spectrophotometric data[5,6,54-72] but also of results obtained by other physical methods: NMR[5,6,72-79] calorimetry[5,6,8,9], dielectric measurements[6,8], etc.

Graphical methods for the simultaneous determination of K and x_C, based on equations of type (III.5)–(III.9), suffer from significant disadvantages, which have been widely discussed in the literature[5,6,8,9,58-73,81]. These are primarily the restriction of their application solely to systems where one 1 : 1 complex AB is formed, i.e. where $p = q = 1$. With increase of p and q, the degree of Eqn. (III.2) increases, which makes it virtually impossible to convert it into a form permitting the construction of linear plots.

Furthermore, the use of equations of type (III.5)–(III.9) yields satisfactory results only subject to the condition $C_C \ll (C_{A_0} + C_{B_0})$. However, in order to test the validity of this condition, it is necessary to know at least the order of magnitude of K; such information is as a rule lacking in the study of new types of complexes. Significant errors in the determination of K and x_C may arise owing to the possible formation in the test system of complexes having compositions other than 1 : 1.

Certain methods of improving the accuracy of the required parameters of the complexes A and B when the use of Eqns. (III.5)–(III.9) leads to large errors for one reason or another have been proposed in a number of studies[82,83]; sometimes attempts were made to employ a computer in order to introduce appropriate corrections[84-86]. For example, in a study of fairly stable 1 : 1 complexes, Tamres and coworkers[82] suggested the use of linear regression models and an iterative procedure in order to refine with the aid of a computer the parameters K and x_C obtained from approximate relations. Such ways of developing computational methods involving the use of approximate equations with subsequent refinement of the parameters obtained are apparently irrational. If the approximations adopted do not satisfy the experimental conditions, it is necessary to employ more rigorous computational methods.

In order to determine the compositions and parameters of complexes A_pB_q which are relatively little dissociated in solution [reaction (II.7)], graphical extrapolation of linear sections of curves obtained by the molar ratios (titration) or continuous variations (isomolar series[1,2,6,]

[12,87,88]) methods is used widely. One then begins with the assumption that the linear sections of $X - C_{B_0}/C_{A_0}$ titration curves (with C_{A_0} = const.; see Fig. 2) or $X-C$ isomolar series curves, where $C = C_{A_0}/(C_{A_0} + C_{B_0})$ (with C = const.; see Fig. 3), correspond to complete binding, i.e. a complete displacement of equilibrium (II.7). This eliminates the necessity for the employment of the non-linear Law of Mass Action equation (II.9) in order to estimate the equilibrium concentrations of the mixture components, which are related solely by the material balance equations (II.20). The composition of the complex and its parameter x_C can be found by extrapolating the linear sections of the experimental curve on the basis of the so-called point of "equivalence"[6] (see Figs. 2 and 3). Knowing x_C it is possible to calculate by Eqns. (II.1) and (III.2) the equilibrium constant for the given reaction from data referring to the part of the experimental curve where the complex dissociates into components (sections KL in Figs. 2 and 3).

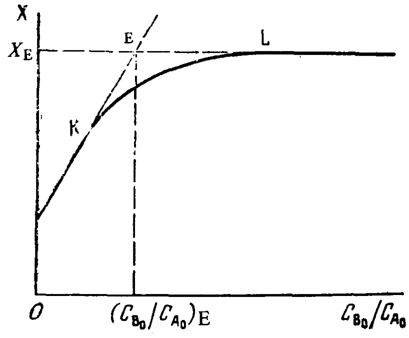

Figure 2. Determination of the composition and parameters of complexes A_pB_q by the titration method. At the equivalence point E we have $(C_{A_0}/C_{B_0})_E = p/q$ and $x_C = (X_E - X_z)p/L(C_{A_0})_E = (X_E - X_z)q/L(C_{B_0})_E$. Along the section KL of the experimental curve, the complex dissociates into components.

A common disadvantage of the method based on linear graphical extrapolation is the absence of a reliable criterion which would make it possible to infer that the condition of the formation in the system of only one complex, which has been adopted in this procedure, does indeed hold. The linearity of sections of the curve, frequently adopted as evidence for the validity of the assumptions made, cannot be regarded as a sufficiently reliable criterion, because, owing to the scatter of experimental points on the graphs, one cannot always detect the curvature which might be a sign of the formation of more than one complex in the system[6,84,85].

If several complexes having different compositions are formed simultaneously in the system, the problem of the determination of their parameters becaomes extremely more complex. The conversion of the computational equations into a form suitable for linear graphical extrapolation or calculation by hand then requires even more drastic approximations than those quoted above for single-stage reactions. In the interpretation of the results of the study of multistage complex-formation reactions it is frequently assumed that, under particular experimental conditions, the solution or vapour contains mainly only one of the complexes formed[1,2,6,12,89-99]. However, this hypothesis can be valid only in relation to complexes with limiting compositions, i.e. complexes containing the maximum or minimum number of the molecules of A and B. The latter is sometimes achieved in the presence of a large excess of the corresponding initial component.

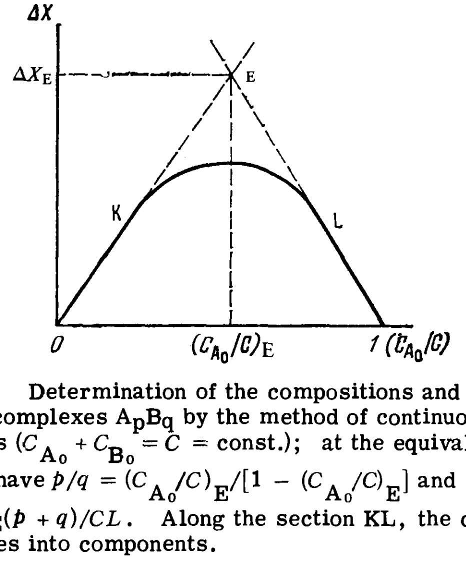

Figure 3. Determination of the compositions and parameters of complexes A_pB_q by the method of continuous variations ($C_{A_0} + C_{B_0} = C$ = const.); at the equivalence point we have $p/q = (C_{A_0}/C)_E/[1 - (C_{A_0}/C)_E]$ and $x_C = \Delta X_E(p + q)/CL$. Along the section KL, the complex dissociates into components.

The available approximate methods for the interpretation of the results of the study of multistage complex-formation reactions are as a rule extremely cumbersome and insufficiently reliable[1,2,6,12,89-95]. We believe that the use of a computer in order to simplify and refine approximate methods of calculation[90,91,98,99] is undesirable, because computer technology permits a rigorous solution of the problems under consideration.

IV. METHODS FOR THE DIRECT SOLUTION OF THE SYSTEM OF EQUATIONS RELATING THE PARAMETERS OF COMPLEXES TO EXPERIMENTAL DATA

Owing to the approximations adopted in the derivation of the corresponding equations, the linear graphical extrapolation methods discussed in the previous section are applicable solely in the study of either comparatively weak or extremely strong complexes. The interpretation of the results of the physicochemical study of complexes of the most common type, i.e. with moderate stabilities, requires the use of more rigorous computational methods.

For single-stage complex-formation reactions, methods for the solution of the system of four equations, comprising Eqns. (II.1), (II.9) and two equations (II.20) without the introduction of any approximations, have been examined[100–118]. Simultaneous solution of these four equations eliminates the equilibrium concentrations of mixture components, which depend on the experimental conditions (c_A, c_B, c_C), and yields only one equation [Eqn. (IV.1)], which contains two unknowns (x_C and K) and the experimental data (X, C_{A_0}, and C_{B_0}):

$$K=\frac{\Delta X/\Delta x}{(C_{A_0}-p\Delta X/\Delta x)^p\,(C_{B_0}-\Delta X/\Delta x)^q}\,. \qquad \text{(IV.1)}$$

In principle, the solution of two equations (IV.1) for two experimental points makes it possible to find the parameters x_C and K.[100] However, the possible experimental errors necessitate the determination of the parameters x_C and K on the basis of data referring to a number of experimental points significantly larger than two. It is necessary to solve a system of non-linear equations (IV.1) for all the pairs of experimental points[100–105]. This method of solution is extremely cumbersome and in practice is possible only with the aid of a computer[100,102]. For the simplest case with $p = q = 1$, methods have been proposed[106–116] for the determination of the parameters x_C and K which replace the procedure involving the solution of a system of non-linear equations (IV.1). Having specified an arbitrary set of values of one of the parameters to be determined, the second parameter is determined from experimental data. Eqns. (IV.1) are then written in a form convenient for the calculation of one parameter from the specified values of the other:

$$K=\frac{\Delta X/\Delta x}{(C_{A_0}\Delta x-\Delta X)\,(C_{B_0}\Delta x-\Delta X)}\,, \qquad \text{(IV.2)}$$

$$x_K=x_A+x_B+\frac{\Delta X}{2L}/(R-\sqrt{R^2-4C_{A_0}C_{B_0}}), \qquad \text{(IV.3)}$$

where $R = C_{A_0} + C_{B_0} + 1/K$.

The solution of the problem is found by studying the relation $K = f(x_C)$ or $x_C = f'(K)$, or $K = \varphi(C_{A_0}, c_{B_0})$, or $x_C = \varphi'(C_{A_0}, C_{B_0})$. Bearing in mind that the system must have a unique solution for x_C and K, these parameters can be found graphically from the coordinates of the points of intersection of the lines of the $K = f(x_C)$ or $x_C = f'(K)$ series, plotted for each experimental point[106].

Since the equilibrium constants and the physical parameters of the complexes are independent of the experimental conditions, K and x_C may be found by varying arbitrarily one of the parameters until a value is obtained for which the second parameter remains constant regardless of the initial concentrations C_{A_0} and C_{B_0}.[114–116] The last pair of values of x_C and K is a solution of the problem.

Olofson and coworkers[117,118] proposed a method for the solution of Eqn. (IV.1) with $p = q = 1$ on a computer. Eqn. (IV.1) is written as follows:

$$\frac{C_{A_0}C_{B_0}}{\Delta X}\,\Delta x-(C_{A_0}+C_{B_0}+1/K)+\frac{\Delta X}{\Delta x}=\varphi_j=0. \qquad \text{(IV.4)}$$

Values of x_C and K for which the functions φ_j become zero are solutions of Eqn. (IV.4). Owing to experimental errors, the required parameters are found from the pair of values of x_C and K corresponding to the minimum in the function $\sum_{j=1}^{N}|\varphi_j|$, where j and N are the ordinal number of the experiment and the total number of experiments respectively. For complexes A_pB_q with compositions more complex than 1 : 1, the use of such procedures in order to solve equations of type (IV.4) involves considerable difficulties owing to the increasing degree of Eqn. (IV.1).

A method has been proposed[119] for the solution of Eqns. (IV.1) for complexes A_pB_q with any values of p and q by means of the following equation:

$$x_C=px_A+qx_B+\frac{\Delta X}{2LC_{A_0}}\,\frac{a\pm\sqrt{a^2-4bC_{A_0}\Delta X'\,(q\Delta X-C_{B_0}\Delta X')}}{q\Delta X-C_{B_0}\Delta X}\,, \qquad \text{(IV.5)}$$

$$\text{where } a=[p(p-1)C_{B_0}+q(q-1)C_{A_0}]\,\Delta X'+pq\Delta X,$$
$$b=pq(p+q+1),\ \Delta X'=(\partial X/\partial C_{B_0})_{C_{A_0}}-x_BL.$$

Eqn. (IV.5) was obtained by differentiating Eqn. (IV.1) with respect to C_{B_0} subject to the condition $(\partial K/\partial C_{B_0})_{C_{A_0}=\text{const.}}=0$. The derivative $(\partial X/\partial C_{B_0})_{C_{A_0}}$ in Eqn. (IV.5) may be found from the experimental dependence of X on C_{B_0} by any of the known methods for the determination of a derivative with respect to a specified function. Knowing x_C, it is easy to calculate K from Eqn. (IV.1). Such calculations may be performed also by hand, but this requires a considerable amount of time. A program has been devised[43] for calculations by Eqn. (IV.5) on a Minsk-22 (or Minsk-32) computer. The derivatives $(\partial X/\partial C_{B_0})_{C_{A_0}}$ are then calculated by fitting a second-degree polynomial to sections of the experimental $X - C_{B_0}$ curve[43,120]. The use of a computer greatly reduces the time required for calculation.

In the general case of an n-stage complex-formation reaction, the number of equations is $n + 3$: one equation (II.1), n equations (II.9), and two equations (II.20). When the equilibrium concentrations of the mixture components (C_A, C_B, ..., C_1, ..., C_n) are eliminated by the simultaneous solution of these equations, then in principle it is possible to obtain one equation relating the parameters of the complexes x_1, ..., x_n, K_1, ..., K_n to be determined to the experimental X, C_{A_0}, C_{B_0} data. Simultaneous solution of the system of equations for $2n$ experiments makes it possible to find all $2n$ unknowns.

However, with increase of the number of reaction stages and of the complexity of the composition of the complexes formed, there is an increase not only of the number of equations to be solved simultaneously but also of their degree. As a result of this, the rearrangements associated with the elimination of equilibrium concentrations from Eqns. (II.1), (II.9), and (II.20) become much more laborious. Even in the simplest case involving the simultaneous formation of only two complexes, having 1 : 1 and 1 : 2 compositions, the solution of a system of not less than four cubic equations is necessary[100,124,125]. There are no literature data concerning the use of such procedures for the interpretation of the results of studies on complex-formation reactions involving more than three stages[100,121–125].

Thus the procedure involving the direct solution of a system of non-linear equations, particularly in the study of multistage complex-formation reactions (even with the aid of a computer), appears to be relatively unsuitable, primarily because of its extremely cumbersome nature. For a rigorous determination of the parameters of the complexes from physicochemical experimental data, it is apparently more rational to employ computational methods based on the statistical principle of maximum probability.

V. METHODS OF CALCULATION BASED ON THE STATISTICAL PRINCIPLE OF MAXIMUM PROBABILITY

Methods of computer calculations based on the principle of maximum probability[126] consist in seeking a set of parameters x_1, ..., x_n, K_1, ..., K_n to be determined which gives the best description of the experimental data, i.e. the dependence of the measured property of the solution (or vapour) X on the initial concentrations C_{A_0}, C_{B_0}, ... In essence, all these methods reduce to seeking a minimum in the function reflecting the deviation of the experimental quantities X_{exp} from the values X_{calc} calculated by Eqns. (II.1), (II.13), and (II.20) using arbitrarily specified and varied values of the required parameters[127]. The principle of least squares, which is most widely used in such calculations, yields fairly reliable results[12–14,20–47,128–203].

Methods of calculation in accordance with the principle of least squares involve the seeking of a minimum in the function

$$F=\sum_{j=1}^{N}(X_{\text{exp}\,j}-X_{\text{calc}\,j})^2. \tag{V.1}$$

The calculation of the quantity F [Eqn. (V.1)] from the specified set of parameters $x_1, \ldots, x_n, K_1, \ldots, K_n$ consists of three stages.

1. Starting with the specified equilibrium constants $K_1, \ldots, K_n$ and the experimental values of C_{A_0j} and C_{B_0j}, one calculates the equilibrium concentrations of all the mixture components $C_A, C_B, \ldots, C_1, \ldots, C_n$ by the simultaneous solution of the system of non-linear Law of Mass Action equations (II.13), (II.15), or (II.19) and the material balance equations (II.20).
2. Using the values of $C_A, C_B, \ldots, C_1, \ldots, C_n$ obtained and the specified set of physical parameters of the complexes $x_1, \ldots, x_n$, the values of $x_{\text{calc}\,j}$ are calculated from the linear equations (II.2)–(II.6) or (II.1).
3. Having determined the $X_{\text{calc}\,j}$ for all the N experiments and using the corresponding values of $X_{\text{exp}\,j}$, one calculates F by Eqn. (V.1).

By varying the arbitrarily specified set of parameters $x_1, \ldots, x_n, K_1, \ldots, K_n$, one finds a minimum in the function F. As a first approximation, one can use parameters obtained with the aid of approximate methods of calculation. The set to which corresponds a minimum in F is regarded as a probable set of parameters $x_1, \ldots, x_n, K_1, \ldots, K_n$ to be determined.

In order to find the minimum in the function F of $2n$ variables, various methods for seeking an extremum in a function are used[17,204–212]. In particular, in the study of single-stage processes, the simplest method of "trial and error" is sometimes employed[141,142,177,179,195]. The method of successive sorting of variables and the method of "descents along coordinates" are frequently used[147,157,174–176,189]. At the same time, various types of iterative procedures are widely employed to seek the minimum in the function F: gradient methods[33–36,134], Newton's method and its versions (the Newton–Raphson method[14,21–25,37–39] and the Gauss–Newton method[20,27,30–32,40,152,160]), and the Davidson–Fletcher–Powell (DFP) method[41,165].

The function F [Eqn. (V.1)] is "pit-like"[210–212], i.e. near the minimum it is represented by an extended narrow "pit". For this reason, in seeking the minimum in F one frequently employs special so-called "pit mapping" methods[13,43,47,156]. The possibilities and disadvantages of various methods used in seeking the minimum in F are compared in the Table.

The derivatives $\partial F/\partial x_i$ and $\partial F/\partial K_i$ required in the search for the minimum in F are usually calculated by the approximate finite difference method[17,204]. A method involving a rigorous analytical calculation of these derivatives with the aid of Jacobi matrices has been proposed[13,43]. The minimum in F may be sought both with respect to all $2n$ variables[155–157,161,176,195] and with respect to n variables $K_1, \ldots, K_n$.[12–14,22,25,141,147,165–170,185,189]

The fact that the parameters $x_1, \ldots, x_n$ enter into Eqns. (II.1)–(II.6) as coefficients of the equilibrium concentrations of the complexes $c_1, \ldots, c_n$ makes it possible to reduce the number of variables with respect to which the search is made from $2n$ to n. This leads to the possibility of calculating, by the method of least squares which is applicable to linear equations[213], the parameters $x_1, \ldots, x_n$ giving the best description of the experimental data for a specified set of $K_1, \ldots, K_n$.[10,13]

Comparison of the methods for seeking the minimum in F.

No.	Method	Advantages of method	Disadvantages of method
1	Construction of networks of schematic maps (tabulation)	Method is complete and accurate	Requires much computer time
2	Newton–Raphson method	Method requires little computer time	Method does not distinguish saddle points and minima. The quadratic approximation method can be both positively and negatively defined. The region of convergence is small
3	Gauss–Newton method	Method locates only minima. The quadratic approximation matrix is always positively defined. The region of convergence is larger than in method 2	Method requires more computer time than method 2.
4	Davidon–Fletcher–Powell (DFP) method	Method locates only minima. The region of convergence is larger than in methods 2 and 3	Method requires approximately 25% more computer time than method 2. Its computation algorithm is more complex
5	"Pit mapping" method	Method locates only minima. The region of convergence is larger and the "ravine" direction is better defined than in methods 2, 3, and 4. The method requires a smaller amount of computer memory	Method requires more computer time. Near the minimum its execution is slower than that of methods 2, 3, and 4

The required parameters $x_1, \ldots, x_n$ and $K_1, \ldots, K_n$ may differ significantly in magnitude, which complicates the search for the minimum in F and frequently requires a special scaling procedure, which is extremely difficult for the K_i.[129–131] In addition, in seeking $F_{\min}$ some of the values of $K_1, \ldots, K_n$ may fall within the region of negative values, which has no physical significance and this also complicates the search for $F_{\min}$ and requires the use of a special computational algorithm[129,130]. The use of the $\ln K_i$ instead of the K_i as the mapping variables makes it possible to overcome these difficulties[10,12,13,20,23].

In the calculation of the equilibrium concentrations $C_A, C_B, \ldots, C_1, \ldots, C_n$ from the specified $K_1, \ldots, K_n$ the system of equations consisting of n non-linear Law of Mass Action equations and s material balance equations (see Section II) is reduced by simultaneous solution to s equations with s unknown $C_A, C_B, \ldots$ On solving the resulting system of s non-linear equations by one or other iterative procedure[214–216], the values of $C_A, C_B, \ldots$ are found; Newton–Raphson procedure, which is fastest, is most frequently employed for this purpose[22,27,43,215]. It has been suggested in a number of studies[12,22,43] that a satisfactory initial approximation to C_A, C_B, ... required for the iterative method be calculated on a computer for each *j*th experiment by means of special algorithms. On the basis of the values of C_A, C_B, ... obtained, the equilibrium concentrations of the complexes C_1, C_2, ..., C_n are calculated with the aid of the Law of Mass Action equations. The algorithms proposed in the literature for the calculation of equilibrium concentrations are frequently based on the employment of Law of Mass Action equations (II.13) in which the functions f_i or φ_i assume different forms depending on the stoichiometry of each stage of the given reaction. This approach requires the development of individual programs for different types of complex-formation reactions [141-146,153-155,161,173-190,202].

A unique program, applicable to any involved complex-formation reaction, can be devised by resorting to the matrix formulation of the reaction stoichiometry and correspondingly to the Law of Mass Action equations expressed in form (II.15) [14,20-42,156,165,166] or (II.18). [13,43,47,168-170,191,194]

Complexes are studied by various physical methods, so that procedures for the interpretation of experimental results in terms of the principle of least squares and on the basis of specific equations of type (II.2)–(II.6), applicable only to each specific physical method separately, have been developed extensively. Methods have been described for the interpretation of the results of calorimetric [25,28,33,38,161-173], spectrophotometric [22,141-160],

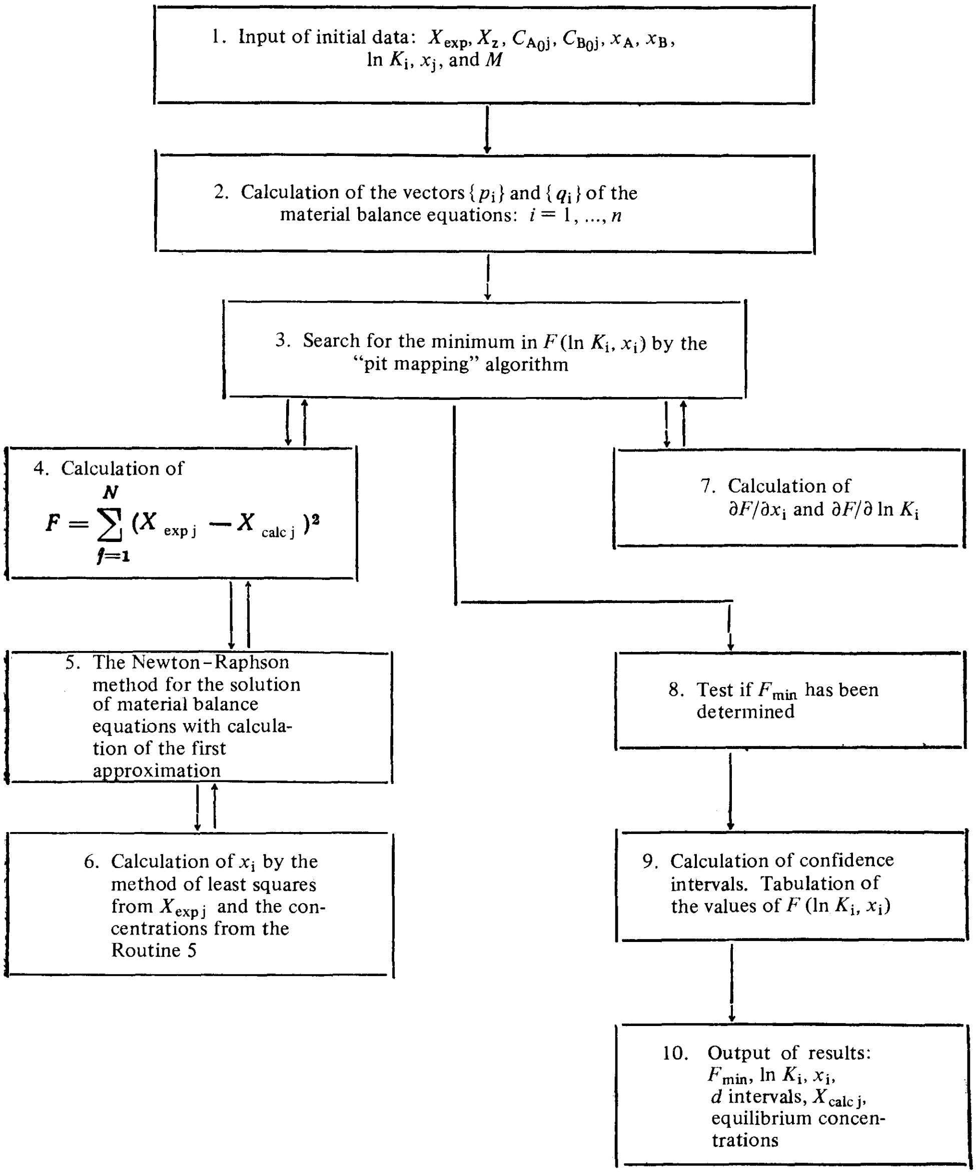

Figure 4. Flow diagram of the computer program for the calculation of the parameters of complexes.

NMR,[14,174-191] dielectric constant[12,192-196], potentiometric[20-23,26-36,39-42,128-140], tensimetric[197-201], and cryoscopic[24,202] measurements. Thus, when several methods are used, a whole library of programs is required. It appears more rational to develop general programs applicable to any research technique.

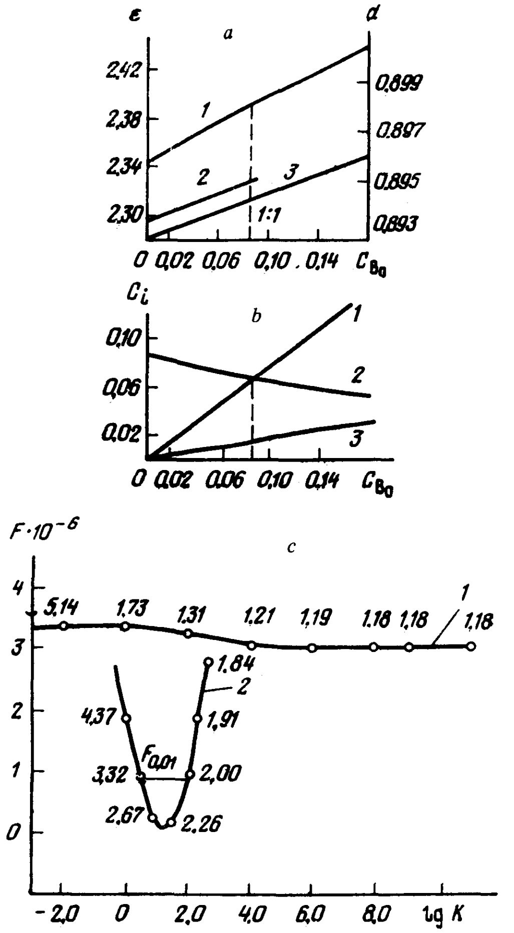

Figure 5. *a*) Experimental $\epsilon - C_{B_0}$ (curves *1* and *2*) and $d - C_{B_0}$ (curve *3*) plots; $B = (C_6H_5)_2S$ [C_{A_0}: 1) and 3) 0.085; 2) 0.028]; *b*) equilibrium concentration distribution diagram [1) $(C_6H_5)_2S$; 2) $TeCl_4$; 3) $TeCl_4.(C_6H_6)_2S$; $C_{A_0} = 0.085$]; *c*) $F = \ln K$ tabulation graphs for a dielectric constant study of the reaction $TeCl_4 + (C_6H_5)_2S \overset{K}{\rightleftharpoons} TeCl_4.(C_6H_5)_2S$ in benzene [C_{A_0}: 1) 0.028; 2) 0.085]; $\ln K = 1.25 \pm 0.75$; $\alpha = 2.4 \pm 0.4$; the numerals opposite the points in the figure represent the values of α; $F_{0.01}$ is the F level for $p = 0.01$.

Such a program, consisting of individual routines, each of which can be used when necessary and can be supplemented by other routines, was proposed for the first time by Sillén and Ingri[22-25,129-131]. A more general and convenient program has been proposed by the present authors[13,43]. The program is based on the general functional relation (II.1), which, as shown above (Section II), is applicable with adequate approximation to the majority of physical methods which are most informative and most widely used in the study of complexes.

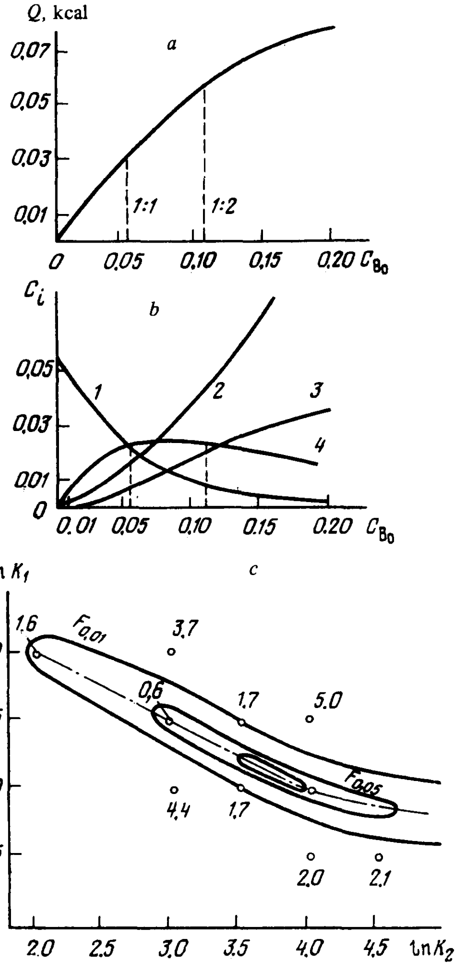

Figure 6. *a*) Experimental $Q - C_{B_0}$ curve; B = $(iso\text{-}C_4H_9)_2SO_2$; *b*) equilibrium concentration distribution diagram ($C_{A_0} = 0.055$) [1) $SnCl_4$; 2) $(iso\text{-}C_4H_9)_2SO_2$; 3) $SnCl_4.2(iso\text{-}C_4H_9)_2SO_2$; 4) $SnCl_4.(iso\text{-}C_4H_9)_2SO_2$; *c*) 10^{-6} F tabulation plot in the $\ln K_1 - \ln K_2$ plane for a calorimetric study of the reactions $SnCl_4 + (iso\text{-}C_4H_9)_2SO_2 \overset{K_1}{\rightleftharpoons} SnCl_4.(iso\text{-}C_4H_9)_2.SO_2$ and $SnCl_4.(iso\text{-}C_4H_9)_2SO_2 + (iso\text{-}C_4H_9)_2SO_2 \overset{K_2}{\rightleftharpoons} SnCl_4.2(iso\text{-}C_4H_9)_2SO_2$ in benzene; F_p are the F levels for $p = 0.01$ and 0.05.

A general computational algorithm was developed on the basis of the general equation for the measured property [Eqn. (II.1)], the matrix formulation of the stoichiometric reaction scheme [Eqn. (II.18)], and the "pit mapping" procedure for seeking the minimum in the function F.

It makes it possible to employ a single program in order to interpret the results of studies on various types of complex-formation reactions by ultraviolet and NMR spectroscopic methods, dielectric measurements, and calorimetric, cryoscopic, and any other methods for which the measured property obeys the rule of additivity of contributions. A brief flow diagram of the program is illustrated in Fig. 4. Together with the parameters $x_1, \ldots, x_n, K_1, \ldots, K_n$ to be determined, the program generates the minimum in F ($F_{\min}$), the values of X_{calc}, and the equilibrium concentrations of the components corresponding to all the points on the experimental curve. The values of $C_A, C_B, \ldots, C_1, \ldots, C_n$ at each point on the experimental $X = f(C_{A_0}, C_{B_0})$ curve can be used to plot diagrams illustrating the distribution of the equilibrium concentrations (Figs. 5*b*, 6*e*, and 7*b*). The values of $X_{\text{calc}\,j}$ make it possible to compare clearly (graphically) the experimental results with the calculation (Figs. 5*a*, 6*a*, and 7*a*). $F_{\min}$ is used to estimate the reliability of the results obtained.

The determination of the parameters $x_1, \ldots, x_n, K_1, \ldots, K_n$ by seeking the minimum in F is not the final stage of the calculation. A necessary condition for the solution of problems on the basis of the statistical principle of maximum probability is the estimation of the reliability of the results. This is particularly important when the functions X are non-linear [Eqn. (II.1)] and when F [Eqn. (V.1)] can have several minima and only one of these must correspond to a unique solution of the problem. Various procedures have been described in the literature[13,33,43,129,161,164] for describing the reliability of the parameters of the complexes obtained. It has been suggested[13,43] that the Fischer statistic be used:

$$\sigma^2/\sigma^2_{\exp} \leqslant F_{\nu_1,\nu_2,p}, \qquad (V.2)$$

where σ and $\sigma_{\exp}$ are the variances of the calculation and the experiment respectively, ν_1 and ν_2 are the numbers of degrees of freedom in the numerator and denominator of Eqn. (V.2), and p is the level of significance of the statistic. This statistic is fairly well founded only for linear problems[126,217-220], but, owing to the lack of other statistics, it is usually employed also for non-linear relations.

The quantity σ may be calculated from $F_{\min}$:

$$\sigma^2 = F_{\min}/(N - 2n). \qquad (V.3)$$

On the basis of Eqns. (V.2) and (V.3), we obtain the condition for the reliability of the results:

$$F_{\min} \leqslant F_{\nu_1,\nu_2,p}\sigma^2_{\exp}(N - 2n),$$

or

$$\tau = F_{\min}/[F_{\nu_1,\nu_2,p}\sigma^2_{\exp}(N - 2n)] \leqslant 1. \qquad (V.4)$$

The validity of condition (V.4) shows that the proposed stoichiometric reaction scheme and the parameters $x_1, \ldots, x_n, K_1, \ldots, K_n$ obtained correspond to the true values with a probability close to $1 - p$, where p is the chosen level of significance (usually $p = 0.01$, 0.05, and 0.5). When the reaction stoichiometry has been incorrectly formulated, the condition (V.4) is not as a rule fulfilled[43,47,168-170,194,221]. Thus the above criterion of reliability can be used to establish the stoichiometry of the reaction investigated.

The confidence limits serve as an indication of accuracy. The determination of confidence limits for $x_1, \ldots, x_n$ and $K_1, \ldots, K_n$ is a fairly complex task. In a number of studies[27,33,36,129,155-157,163] the confidence limits are determined using the information matrix[126,217-220], which is constructed on the basis of the quadratic approximation to the function F at the minimum.

A more rigorous procedure for estimating the confidence limits for the parameters to be determined involves the construction of confidence regions using the Fischer statistics[13,43]. The confidence region (*d* region) is made up of all the sets of parameters satisfying the condition

$$F(x_1, \ldots, x_n, K_1, \ldots, K_n) \leqslant F_{\nu_1,\nu_2,p}\sigma^2_{\exp}(N - 2n). \qquad (V.5)$$

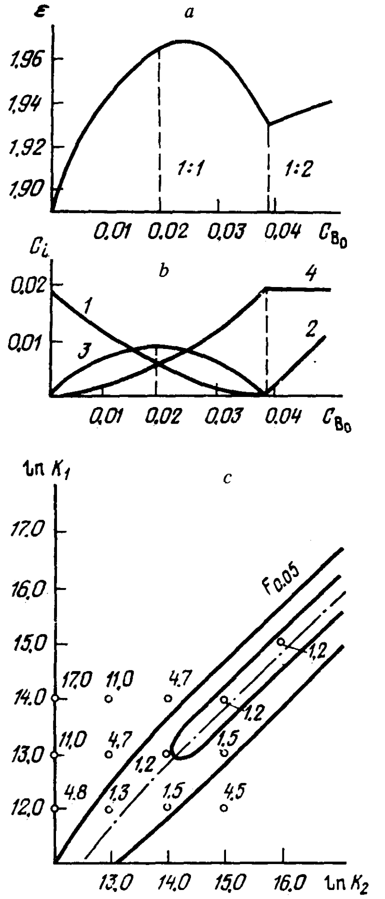

Figure 7. *a*) Experimental $\epsilon - C_{B_0}$ curve; $B = (C_4H_9)_3PO$; *b*) equilibrium concentration distribution diagram (C_{A_0} = 0.019) [1) $SnCl_4$; 2) $(C_4H_9)_3PO$; 3) $SnCl_4.(C_4H_9)_3PO$; 4) $SnCl_4.2(C_4H_9)_3PO$]; *c*) 10^{-5} F tabulation graph in the $\ln K_1 - \ln K_2$ plane for a dielectric constant study of the reactions $SnCl_4 + (C_4H_9)_3PO \overset{K_1}{\rightleftharpoons} SnCl_4.(C_4H_9)_3PO$ and $SnCl_4.(C_4H_9)_3PO_4 + (C_4H_9)_3PO \overset{K_2}{\rightleftharpoons} SnCl_4.2(C_4H_9)_3.PO$ in hexane; $F_{0.05}$ is the F level for $p = 0.05$.

The true values of the parameters are located with a probability $\sim(1 - p)$ within the limits of this region. The standard deviations for the parameters found (the set corresponding to $F_{\min}$) are obtained from the largest and smallest values of each of the required parameters in the *d* region.

d regions can be constructed by a tabulation procedure, i.e. one involving the calculation of F for a series of values of the required parameters varying within the specified region in specified steps. For $n \leq 2$, it is possible to construct tabulation graphs (Figs. 5*c*, 6*c*, and 7*c*) and find the confidence regions by plotting lines corresponding to constant values of F for each of the selected levels of significance. The same procedure can be used to investigate the behaviour of the functions F in the particular region of variation of the mapping variables[13,43,221]. It is noteworthy that the dimensions of the confidence regions and correspondingly of the confidence limits for the parameters obtained are greater the less sensitive the function F to changes in the mapping variables[43,221-225]. The sensitivity of F to mapping variables depends on the amount of information yielded by the experiment[43,225] and, in particular, on the choice of the initial concentrations C_{A_0} and C_{B_0} (see, for example, Fig. 5*c*, curves I and II, and Figs. 6*c* and 7*c*).

Thus the reliability of the results depends both on the reliability of the method of calculation and on the correct formulation of the experiment. Mathematical experimental design methods[223-226] make it possible, in principle, to select the optimum conditions for the experiment. In problems of the determination of the stoichiometric scheme and of the physicochemical parameters of complexes, a successive design is most suitable. It can be achieved in two ways: (1) design for refining the values of the required parameters for a known stoichiometry; (2) design for refining and selecting stoichiometric reaction schemes[224]. It is noteworthy that in problems of the type under consideration mathematical experimental design has not yet found sufficiently extensive applications[224,226].

In the study of two-component systems mathematical treatment of the first series of titration curves and analysis of equilibrium concentration distribution diagrams as a rule make it possible to select the concentration conditions for yet another one or two series of experiments and to obtain fairly reliable results by treating all the experimental data together[43,169,170,221,225].

An effective criterion of the reliability of the physicochemical parameters determined is a satisfactory agreement between the stoichiometric schemes for complex-formation reactions and equilibrium constants for individual stages obtained in the mathematical treatment of the results of studies of the same reactions by several physical methods[6,13,43,155,169,170].

In conclusion it must be emphasised that the development of methods for the mathematical and statistical treatment of experimental results greatly extends the scope of physicochemical studies of complex-formation reactions. In particular the study of multistage reactions and multicomponent systems became possible only after the development of the corresponding computational methods.

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